MERCURY($^3P_1$) SENSITIZED PHOTOREACTIONS OF FURAN: DETAILS OF THE PRIMARY PROCESSES

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INTRODUCTION

In earlier studies[1,2] of the photosensitization of furan vapour by mercury($^3P_1$) atoms, it has been reported that the principal photochemical process is a decarbonylation which has a quantum yield of 0·4 at a pressure of furan of a few mm Hg. The C_3 fragment which was simultaneously produced was found to consist of a mixture of cyclopropene and methylacetylene. At high conversions, some allene was also formed presumably by a secondary process.

A study[2] of the minor products formed in this system, especially at 1 atm pressure, indicated that on sensitization by $Hg(^3P_1)$ atoms furan was capable of undergoing Diels–Alder addition with quantum yields of the order of a few per cent, and that the adducts corresponded to (I), (II), and (III). The identification of (III), which is the Diels–Alder adduct of furan to

$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$
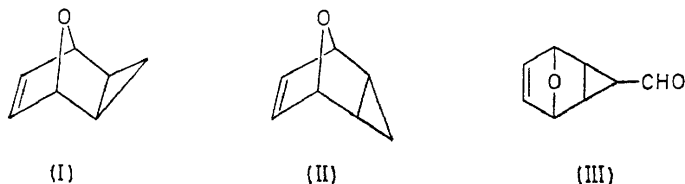
2-cyclopropenecarboxaldehyde, suggested that the latter may be the initial product of the rearrangement of furan according to Eq. (1). Subsequent decarbonylation of 2-cyclopropenecarboxaldehyde appeared to be a

$$\tag{1}$$

$$\tag{2}$$
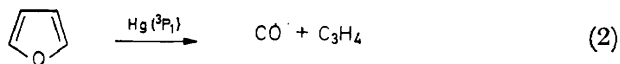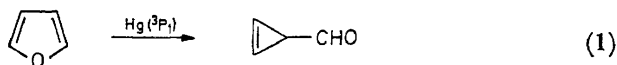
plausible route to the over-all reaction (2). Further aspects of this mechanism will be considered in the discussion.

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In this investigation (i) attempts have been made to identify reactive intermediates in the furan: $Hg(^3P_1)$ system by infrared spectroscopy, (ii) the pressure dependence of reaction (2) and the effect of various additives on (2) have been studied, and (iii) the direct irradiation of furan in the condensed phase in an inert solvent in the presence and absence of molecules with reactive groups has been carried out.

EXPERIMENTAL

Materials

Furan (Quaker Oats Company) was fractionated on a 24-plate spinning-band column. A narrow cut which boiled constantly at 31° (uncorr.) was collected. It was admitted to a vacuum line, degassed repeatedly at $-78°$, and used. No impurities were seen in the sample by vapour phase chromatography. The additive materials used were commercial samples of the highest purity available.

Apparatus and procedure

Quantitative studies of pressure dependence and the effects of additives were carried out in a 1·1 litre cylindrical quartz cell which was illuminated by three 8-watt low pressure mercury resonance lamps. The lamps were calibrated with a uranyloxalate actinometer. The intensity of the mercury resonance line at 2537 Å was of the order of 10^{16} photons/ml/min. At the end of each run the cell was flamed in the presence of air to burn away any polymer on the wall. A drop of mercury was added and the cell was evacuated before furan vapour was introduced. Thoroughly shaking the cell before irradiation served to mix the mercury vapour with furan. Conversions were kept to less than 5 per cent in order to avoid effects such as the local depletion of mercury vapour and the diminution in the intensity by the filtering action of the polymer film that was formed on the wall. The yield of CO was reproducible to ± 5 per cent over a period of several months.

Analysis for CO was carried out by a conventional distillation at liquid nitrogen temperature. Analysis for total C_3, methylacetylene, and cyclopropene was conducted by admitting a small vapour sample from the cell to the gas sampling valve of a gas chromatograph. Only relative values for total C_3 were obtained. A 3-metre column of tetraisobutylene at room temperature was capable of separating methylacetylene, cyclopropene, and allene from each other and from the other products. As noted previously[1], the yield of the C_3 products was always less than that of the CO obtained. This is not surprising as C_6 products presumably from the dimerization of C_3 fragments, and C_7H_8O products from the addition of furan to C_3H_4 were readily identifiable at even a few cm pressure and low conversions.

Infrared spectroscopy of the transient intermediates in the system was conducted in a 10 cm long quartz cell which was closed with sapphire windows. The cell was filled with furan vapour and a drop of mercury, and illuminated with one 8-watt mercury resonance lamp at 5 cm. Spectra were recorded with a Perkin–Elmer 336 Infrared Spectrometer.

Irradiations in solution were carried out in quartz test tubes of 1 cm diam. and 20 cm long. Mercury resonance radiation from 16 General Electric 8-watt lamps was used.

RESULTS

In *Table 1*, the effect of furan pressure on the products of the decarbonylation process is presented. In *Table 2*, the effect of four added gases on the decarbonylation process is listed.

Table 1. Influence of pressure on yield of decarbonylation products
(mercury resonance radiation at 2537 Å; room temperature; cell volume, 1·1 litre)

Furan pressure (mm)	Time (min)	CO (μmole/min)	Cyclopropene / ΣC_3	ΣC_3 (relative yield)
263·0	15·0	9·32	0·769	2·54
196·3	10·0	12·47	0·733	3·20
144·8	5·0	15·50	0·727	6·30
130·0	1·7	15·80	not determined	not determined
78·2	5·0	16·77	0·590	7·61
67·5	3·0	19·58	0·573	(5·35)
37·6	1·0	22·01	0·455	8·76
24·1	1·0	25·61	0·343	8·75
13·0	0·8	25·00	0·295	7·24
7·3	0·5	25·82	0·225	5·52
5·1	0·5	21·48	0·211	5·80

Table 2. Effect of additives on the sensitized decarbonylation of furan
(mercury resonance radiation at 2537 Å; room temperature)

Furan (mm Hg)	Added gas	Gas pressure (mm)	Time (min)	CO (μmole/min)	Cyclopropene / ΣC_3	ΣC_3† (relative yield)
165·0	Allene	28·8	10	9·76	not determined	not determined
62·5	Oxygen	4·2	3	not determined	0·476	3·5
76·6	Cyclopentene	18·9	5	13·37	0·617	5·3
137·0	Methanol	37·0	5	13·58	0·729	3·1

† These values are in the same units as the relative yields of ΣC_3 in *Table 1*.

In *Figure 1*, the infrared spectrum of a sample of furan vapour before and after sensitization by Hg($^3P_1$) atoms is presented as a function of time.

Irradiation of furan in cyclopentane (20 per cent) solution gave rise to no detectable volatile products. A yellow solid readily settled out as the irradiation proceeded. This solid could be isolated by filtration. Its infrared spectrum is shown in *Figure 1*. Since it was insoluble in any of the common solvents, its molecular weight and analysis could not be determined.

Irradiation of furan in cyclopentane (20 per cent) solution in the presence of methanol (10 per cent) or cyclopentene (10 per cent) failed to yield the adducts detected in the sensitized reaction in the vapour phase.

DISCUSSION

Nature of the excited state

The extinction coefficient of furan vapour at 2537 Å is so small[3] in comparison to mercury vapour[4] that even at 1 atm of furan pressure at 31° (the
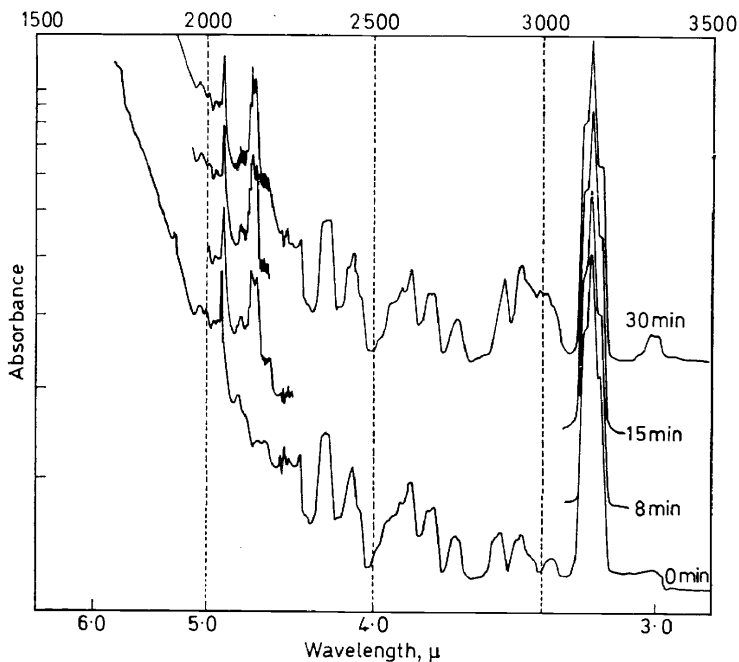
Figure 1. Infrared spectrum of furan after photosensitized decomposition

b.p. of furan) it is unlikely that a significant portion of the incident resonance radiation is absorbed by furan molecules. If all of the photochemistry observed is due to sensitization by $Hg(^3P_1)$ atoms, then the excited state of furan responsible for it will be the triplet, assuming that spin is conserved in the energy transfer process.

$$Hg(^1S_0) + h\nu \ (2537) \longrightarrow Hg(^3P_1) \tag{3}$$

$$Hg(^3P_1) + F \longrightarrow Hg(^1S_0) + F^* \tag{4}$$
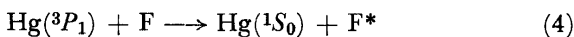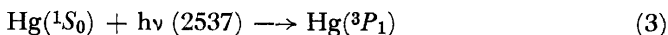
Since there is no information in the literature on the triplet level(s) of furan, we shall merely assume that only one electronically excited state of furan is involved in the photochemical processes reported here, and further will refer to this excited state by the noncommittal symbol F*.

Pressure dependence

The most significant evidence for the intermediacy of an electronically excited state of furan (F*) is the effect of an increase in pressure on the yield of carbon monoxide (*Table 1*). Since the absorbed intensity may be taken to be constant, the rates and hence the quantum yields for CO are seen to decrease continuously with increasing pressure. This suggests a deactivating step such as is given in Eq. (5). The principal chemical reaction

$$F^* + F \longrightarrow 2 F \tag{5}$$

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of F* is undoubtedly the decarbonylation process since this has a quantum yield that is as high as 0·4[1]. It has already been indicated that the reaction proceeds in two steps (Eqs. 6 and 7), the formation of 2-cyclopropene-carboxaldehyde being the initial reaction (Eq. 6). The chemical evidence

$$F^* \longrightarrow \text{▷—CHO}^\dagger \tag{6}$$

$$\text{▷—CHO}^\dagger \longrightarrow \text{▷} + CO \tag{7}$$
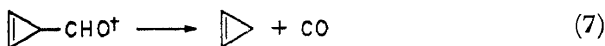
for reaction (6) has been mentioned before. The presence of an intermediate can also be inferred from the kinetic evidence in *Table 1*. If all of the 2-cyclo-propenecarboxaldehyde formed in reaction (6) disappears solely in reaction
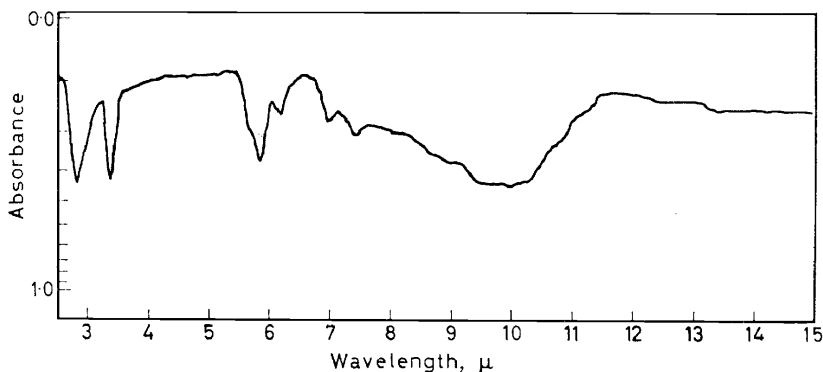

Figure 2. Infrared spectrum (KBr disc) of solid product from irradiation of furan in cyclopentane solution

(7) then the presence of an intermediate is kinetically unnecessary, enabling us to derive Eq. (8). This corresponds to a simple Stern–Volmer mechanism

$$1/\Phi_{CO} = k_5[F]/k_6 + 1 \tag{8}$$

for the quenching of the formation of CO. In *Figure 3* the reciprocal of the rate of production of CO, which in this case is proportional to the reciprocal of the quantum yield, is plotted against the pressure of furan. The line shows a distinct curvature over the whole range of pressure. If it is postulated that the intermediate formed in reaction (6) is capable of undergoing a bimolecular reaction to give products other than CO as in reaction (9),

$$\text{▷—CHO}^+ + F \longrightarrow \text{products} \tag{9}$$
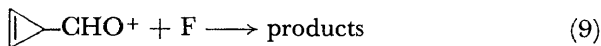
then by the assumption of stationary-state conditions, Eq. (10) can be derived.

$$1/\Phi_{CO} = \{k_7 + k_9[F]\} \{k_6 + k_5[F]\}/k_6k_7 \tag{10}$$

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This relation, which requires that the plot of $1/\Phi_{CO}$ *vs.* [F] be a parabola, clearly is in better agreement with the experimental curve. It can hence be inferred that the decarbonylation of excited furan molecules (F*) proceeds through an intermediate which can be trapped by collisions with furan molecules some of the time.
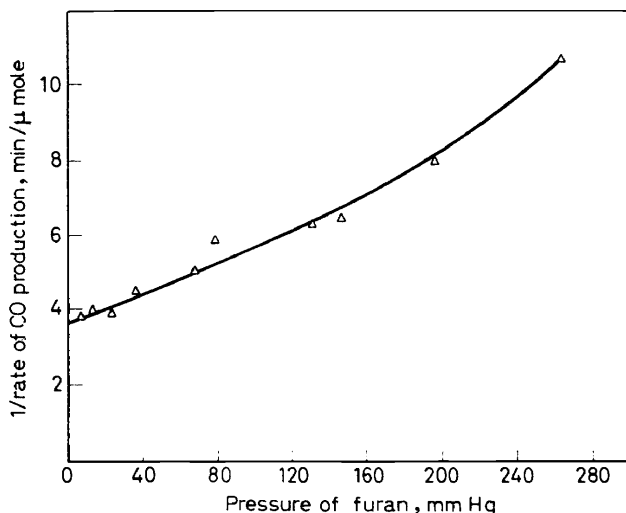

Figure 3. Reciprocal of the rate of CO production *vs.* furan pressure

The formulation of Eq. (6) to give an *excited* 2-cyclopropenecarboxaldehyde deserves some elaboration. The formation of C_3 products is clearly not scavenged by the addition of oxygen as is shown by the data in *Table 2*. Oxygen is more effective than cyclopentene or methanol in decreasing the yield of C_3 products, but since the reactant is a triplet molecule (furan), oxygen can be expected to quench this species to some extent†. The failure
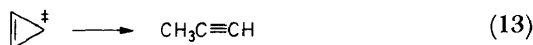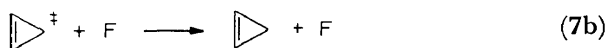

$$(11)$$

$$(12)$$
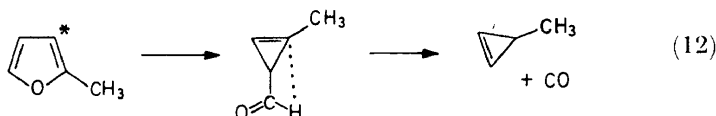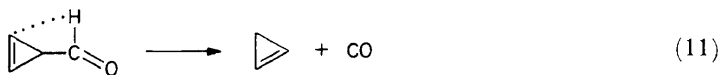
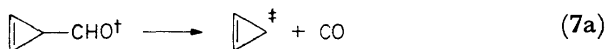of oxygen to eliminate the C_3 products strongly indicates that these products are not formed by a free-radical process but by an intramolecular route such as (11). This would also explain the formation of 3-methylcyclopropene as

† It is relevant to note that oxygen scavenges the $n \rightarrow \pi^*$ triplet state of carbonyl compounds very efficiently but is not so effective with the triplet states of hydrocarbons or olefins.

the principal product in the Hg($^3P_1$) sensitized decomposition of 2-methyl-furan[1]. Since it is the carry-over of energy from reaction (6) that must provide the activation for (7), it is probable that the 2-cyclopropenecar-boxaldehyde is "hot".

The data in *Table 1* show that the yield of C_3 products parallels that of CO in the pressure range from 24 to 263 mm. At lower pressures, the yield of CO levels off whereas the yield of C_3 dips once again. Over the entire pressure range the yield of cyclopropene relative to the total yield of C_3 products (essentially methylacetylene + cyclopropene) is also seen to be a function of pressure. Since the thermal decomposition of cyclopropene is known to give methylacetylene[5], it is probable that reaction (7) initially gives a "hot" cyclopropene which, unless it is deactivated by collisions, isomerizes to methylacetylene. The situation is entirely similar to the photodecomposition of cyclobutanone wherein cyclopropane and propylene bear a similar relationship[6].

From the elementary reactions (7a), (7b) and (13)

$$\text{▷—CHO}^\dagger \longrightarrow \text{▷}^\ddagger + \text{CO} \tag{7a}$$

$$\text{▷}^\ddagger + \text{F} \longrightarrow \text{▷} + \text{F} \tag{7b}$$

$$\text{▷}^\ddagger \longrightarrow \text{CH}_3\text{C}\equiv\text{CH} \tag{13}$$

it can be readily derived that

$$\frac{\text{rate of formation of } \Sigma C_3}{\text{rate of formation of cyclopropene}} = \frac{k_{13}}{k_{7b}[\text{F}]} + 1 \tag{14}$$

It is important to note that this derivation does not depend on any assumption concerning the nature of the intermediate species from which carbon monoxide and "hot" cyclopropene are formed. In *Figure 4* a plot of the rate of formation of ΣC_3/rate of formation of cyclopropene *vs.* 1/pressure is presented. The plot is linear over the pressure range from 263·0 to 24·1 mm. The value of the intercept which is 1·10 may be considered to be in reasonably good agreement with Eq. (14). It should be pointed out that this fit of Eq. (14) does not prove that (7a), (7b), and (13) form a unique mechanism to explain the pressure dependence of the formation of cyclopropene. An equation of the same form with unit intercept can be derived based on two levels of excitation of 2-cyclopropenecarboxaldehyde, one of which gives methylacetylene and the other cyclopropene. A collision degrades the aldehyde from one level to the other. The objections to this mechanism are: (i) it is unlikely that a reactive molecule such as 2-cyclopropenecarboxalde-hyde, especially with excess excitation energy, can undergo collisions with furan without undergoing a chemical reaction as well, and (ii) the mechanism takes no account of the thermochemical relationship between cyclopropene and methylacetylene.

At pressures less than about 25 mm, the mechanism consisting of (3), (4), (5), (6), (7a), (7b), and (14) seems to be inadequate. This is seen in the rate of formation of CO reaching an almost *constant* value, (ii) the deviation from linearity in the plot in *Figure 4*, and (iii) the decrease in the total
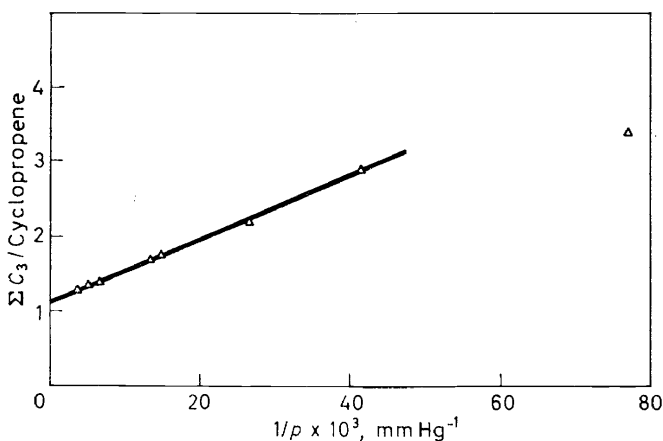

Figure 4. ΣC_3/cyclopropene *vs.* 1/furan pressure

yield of C_3 products with a decrease in pressure. Since wall effects can be expected to become important at pressures less than 10 mm, it is not profitable to speculate about the causes for these deviations.

An interesting point about the secondary reactions in this system is whether the formation of the adducts (I), (II), and (III) by Diels–Alder addition involves an excited furan molecule (F*) or not. The reaction between cyclopentene and furan reported[2] already leaves no doubt that the Diels–Alder addition, *in that instance*, is photosensitized. It was also observed that even in the presence of cyclopentene the adducts (I) and (II) were formed in yields comparable to that of the adduct of cyclopentene although the ratio of cyclopropene to cyclopentene, in the vapour phase, was 1 to 30 or less. It has already been argued that both 2-cyclopropenecarboxaldehyde and cyclopropene are formed in a "hot" state in this system. It is hence possible that the adducts (I), (II), and (III) are formed by the reaction of furan in a ground state and an activated dienophile. Thus the reactions (9) and (7b) could lead to these products.

Infrared spectroscopic studies

Earlier it had been suggested on the basis of chemical evidence that in addition to 2-cyclopropenecarboxaldehyde, another intermediate in the mercury ($^3P_1$) sensitized reactions of furan, although of considerably less importance, may be vinylketene[1,2]. The infrared studies conducted here were chiefly aimed at obtaining some direct evidence for both these intermediates. It can be seen from *Table 2* that the addition of methanol to the system has only a small effect on the production of carbon monoxide. It

suggests that these two intermediates may originate from the electronically excited state *via* independent pathways†.

In the infrared spectra in *Figure 1*, which were obtained at very low conversions, the only new absorption evident after irradiation is a pair of peaks at 2163 and 2146 cm^{-1} which can be attributed to carbon monoxide[7]. The complete absence of any other new absorption between 2100 and 2000 cm^{-1} indicates that vinylketene does not build up to any significant extent in the system. To the extent that the windows of the cell transmitted the radiation of frequency less than 1800 cm^{-1} it can also be stated that any carbonyl absorption due to 2-cyclopropenecarboxaldehyde is also negligible. It is likely that both these intermediates can be stabilized if the irradiation is carried out on a sample in an inert matrix at low temperature. Such experiments are now in progress.

Irradiation of furan in solution

It is known that direct irradiation of furan with light of wavelength down to 2100 Å also leads to decarbonylation as the principal process although the C_3 fragment does not contain any cyclopropene[8]. It is surprising that in the condensed phase, on direct irradiation, there is no detectable yield of low molecular weight products from furan. The infrared spectrum of the polymer (*Figure 2*) indicates a strong carbonyl absorption at 1715 cm^{-1} which does not seem to be due to an aldehyde group. The simultaneous presence of a strong —OH absorption suggests that furan may isomerize under these conditions as in the gas phase (perhaps with a low quantum yield because of the quenching effect of the medium) but that the product undergoes condensation reactions rapidly. Once again matrix studies at low temperatures may help to explain these observations.

ACKNOWLEDGEMENT

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† It has been suggested that the structures (IV) and (V) were reponsible for the production of vinylketene and 2-cyclopropenecarboxaldehyde, respectively, while the struture (VI)
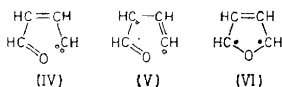
was the reactant in the photosensitized Diels–Alder addition[2]. Although (IV), (V), and (VI) are resonance structures, they do not appear to be interconvertible. This can be explained if (IV) is a triplet electronically excited state while (V) and (VI) occur in the vibrationally excited ground state that is formed by internal conversion. Thus in the condensed phase (i.e. at very high pressures) the formation of carbonyl products is observed but there is no evidence for (photo) Diels–Alder addition or ester formation. The simultaneous formation of products from two or more of the structures (IV), (V) and (VI) thus appears reasonable.

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