Thermal Decomposition of Diazodiphenylmethane catalysed by Sulphur Compounds in the Presence of Oxygen

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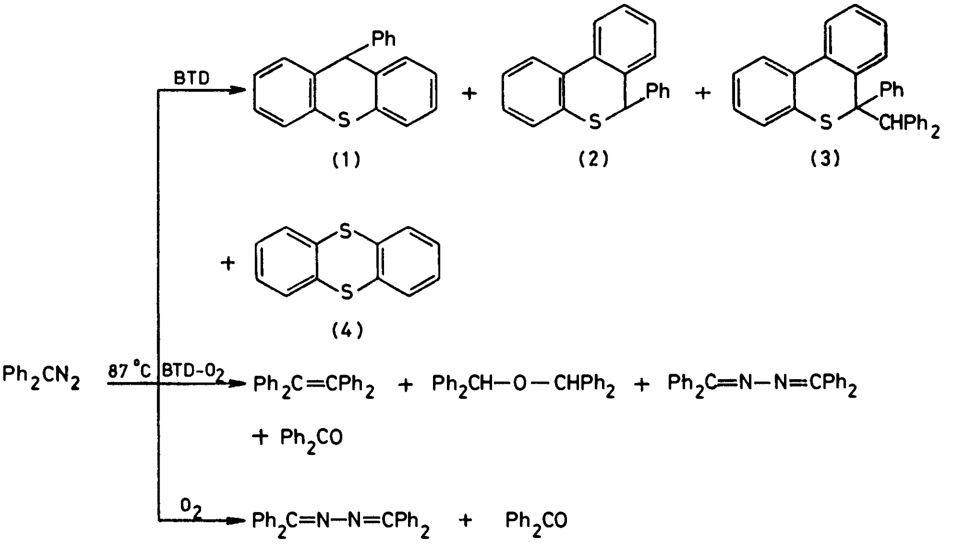
Thermal decomposition at 80 °C of diazodiphenylmethane in oxygen-saturated chlorobenzene in the presence of sulphur compounds (5)—(8) affords tetraphenylethylene, benzophenone, benzophenone azine, as well as small amounts of bisdiphenylmethyl ether. Kinetic and product studies indicate that chain decomposition of the diazoalkane takes place in the presence of sulphides (5)—(8), in competition with unimolecular decomposition leading to diphenylcarbene. Evidence has been obtained that the extent of the chain reaction increases linearly with increasing the concentration of added sulphide and is somewhat dependent on the nature of the sulphur compounds (5)—(8), which appear to exert only a catalytic effect. Addition of n-butanol to chlorobenzene leads to increase in the rate of the chain process at low alcohol concentrations (0.1—0.5M) with formation of large amounts of diphenylmethyl n-butyl ether and suppression of tetraphenylethylene, but no occurrence of the chain decomposition reaction is observed at alcohol concentrations > *ca.* 5.0M. Results are rationalized in terms of reaction of the initially formed diphenylcarbene with oxygen and sulphides (5)—(8), affording some species capable of acting as initiator of the chain decomposition of the diazoalkane, in which the chain carrier might be the diazoalkane radical cation, $Ph_2CN_2^{+\cdot}$

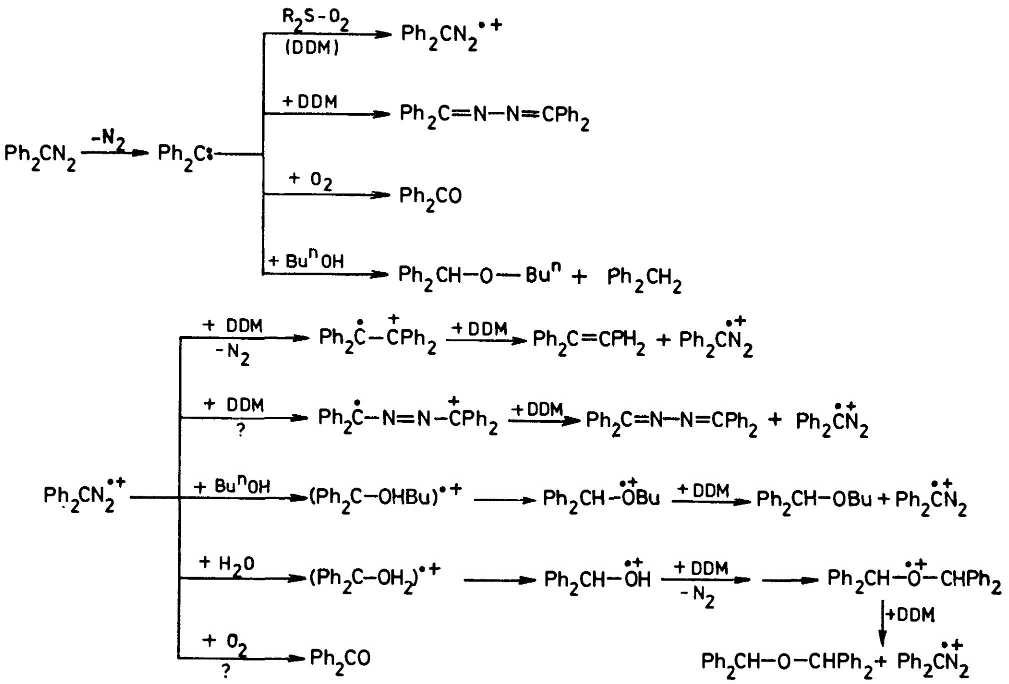
IN a previous paper [1] we reported a study of the reactivity of diazodiphenylmethane (DDM) towards 1,2,3-benzothiadiazole (BTD). Thermal decomposition of DDM at 87 °C in chlorobenzene solution in the presence of BTD afforded 9-phenylthioxanthen (1), 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (2), 6-diphenylmethyl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (3), and thianthren (4) as well as benzophenone azine (BFA) and benzophenone (BF) (Scheme 1). Evidence was obtained that products (1)—(4) arise by preliminary attack on the sulphur atom of BTD by triplet diphenylcarbene leading to decomposition of the heterocyclic nucleus with loss of nitrogen and formation of a diradical intermediate responsible for the observed products. In the course of this investigation we observed that, in the absence of oxygen, disappearance of DDM follows a kinetic law first order in DDM with a rate coefficient which is practically unaffected by the presence of added BTD. However, the presence of oxygen was found to cause a dramatic change both in kinetic and product pattern. In fact thermal decomposition of DDM in chlorobenzene carried out under oxygen in the presence of equimolar amounts of BTD showed a kinetic pattern characteristic of autocatalytic reactions; moreover the reaction led to the formation of tetraphenylethylene (TFE) as major product and small amounts of bisdiphenylmethyl ether (DBE) as well as benzophenone azine and benzophenone. Total suppression of the products (1)—(4) was observed in such conditions.

As expected, in the absence of BTD oxygen was found not to affect the rate of decomposition of DDM, benzophenone, and benzophenone azine being the almost exclusive products in such case (Scheme 1).

These findings prompted us to undertake a study of the thermal decomposition of DDM under oxygen in the presence of a number of sulphur compounds. It appeared to us of interest to ascertain whether and to what extent sulphur compounds are generally capable of



SCHEME 1



Scheme 2

exhibiting an effect analogous to that observed with BTD. We also hoped to throw some light on the mechanism of this apparently catalysed reaction from a detailed kinetic and product investigation.

RESULTS

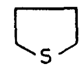
Kinetic Determinations.—The rate of decomposition at 80 °C of DDM was determined in oxygen-saturated anhydrous chlorobenzene solutions of DDM (0.05M) containing equimolar amounts of dibenzyl sulphide (5) (DBS), benzyl phenyl sulphide (6) (BFS), thiolan (7) (TL), and 1,2,3-benzothiadiazole (8) (BTD), respectively. In all cases examined, plots of ln[DDM]$_0$/[DDM] against time pointed clearly to autocatalytic decomposition of DDM, the rates becoming apparently first-order in DDM after an initial stage in which increase in the rate of diazoalkane decomposition occurred. This trend would indicate that unimolecular decomposition of DDM leading to diphenylcarbene takes place in competition with a chain decomposition induced by the presence of sulphides and oxygen. The progressive incursion of the chain decomposition mechanism observed in the initial stage can be ascribed to a progressive increase in the chain carrier concentration, which rises initially, reaches a maximum, and then becomes constant, at which stage disappearance of DDM obeys a first-order kinetic law in diazoalkane, with rate coefficients, k_2, resulting from addition of the two terms, k_1, the rate coefficient of unimolecular decomposition leading to diphenylcarbene and k_{cat}, the rate coefficient of the chain decomposition reaction (k'_{cat}) × the steady chain carrier concentration [equation (1)].

$(PhCH_2)_2S$

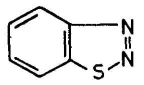
(5)

$PhCH_2SPh$

(6)



(7)



(8)

$$k_2 = k_1 + k'_{cat}[\text{chain carrier}] = k_1 + k_{cat} \qquad (1)$$

The influence of the presence of sulphur compounds (5)—(8) on the rate of decomposition at 80 °C of DDM in oxygen-saturated chlorobenzene can be inferred from data in Table 1, which contains the observed first-order rate coefficients (k_2) as well as the corresponding k_{cat} values, calculated from equation (1), and k_{cat}/k_1 ratios.

Table 1

Observed first-order rate coefficients for thermal decomposition at 80 °C of DDM (0.05M) in oxygen-saturated chlorobenzene in the presence of sulphur compounds (0.05M)

Sulphide	k_1/min^{-1}	k_2/min^{-1}	k_2-k_1 (k_{2cat})	k_{cat}/k_1
None	0.0069			
BTD		0.034	0.027	3.9
TL		0.027	0.020	2.9
BFS		0.045	0.038	5.5
DBS		0.560	0.553	80.1

The effect of the concentration of the sulphur compound on the rate of decomposition of DDM was investigated by carrying out experiments with chlorobenzene solutions of DDM (0.05M) in the presence of varying amounts of BTD (0.005—0.20M). Results in Table 2 show a linear dependence of k_{cat} values on the sulphur compound concentration. From the k_{cat}/k_1 ratios reported in Tables 1 and 2 it can be observed that the extent of the chain decomposition mechanism in the thermal decomposition of DDM depends on the nature and concentration of the added sulphide and it can prevail over unimolecular decomposition even at low sulphide/DDM ratios.

In all experiments performed sulphur compounds (5)—

TABLE 2

Observed first-order rate coefficients for thermal decomposition at 80 °C of DDM (0.05M) in oxygen-saturated chlorobenzene in the presence of varying amounts of BTD

[BTD]/M	k_1/min^{-1}	k_2/min^{-1}	k_2-k_1 (k_{cat})	k_{cat}/k_1
0	0.0069			
0.005		0.0092	0.0023	0.33
0.05		0.034	0.027	3.9
0.20		0.120	0.113	16.4

(8) were recovered unchanged at the end of the reaction, thus pointing to their catalytic effect in the formation of the species responsible for the autocatalytic process. The effect of addition of n-butanol on the rate of decomposition of DDM in the presence of oxygen and DBS (0.005M) was also investigated. Kinetic results are reported in Table 3. A progressive increase in the concentration of added n-butanol causes rate coefficient ratios k_{cat}/k_1 to rise initially, pass through a maximum (at an n-butanol concentration of *ca.* 0.5M), and then fall. At n-butanol concentrations >5.0M, the rates of disappearance of diazoalkane were identical within experimental error to those observed for the corresponding reactions carried out in the absence of DBS.

TABLE 3

Observed first-order rate coefficients for thermal decomposition at 80 °C of DDM (0.05M) in oxygen-saturated chlorobenzene–n-butanol mixtures in the absence and in the presence of DBS (0.005M)

[BuOH]/M	k_1/min^{-1} [a]	k_2/min^{-1} [b]	k_2-k_1 (k_{cat})	k_{cat}/k_1
0	0.0069	0.066	0.059	8.5
0.2	0.0080	0.170	0.162	20.2
0.5	0.0085	0.260	0.251	29.5
1.0	0.0088	0.090	0.081	9.2
2.0	0.0092	0.023	0.014	1.5
5.0	0.0145	0.0146	0	0
10.0	0.0147	0.0145	0	0

[a] Referred to reactions carried out in the absence of DBS.
[b] Referred to reactions carried out in the presence of DBS.

In the absence of DBS the thermal decomposition of DDM in oxygen-saturated chlorobenzene–n-butanol mixtures was found to be of first order through the range of n-butanol concentration employed. A slight variation of the rate coefficient (k_1) was observed over the range of alcohol concentration in agreement with related results reported for the thermal decomposition of diazo-4,4′-dichlorodiphenylmethane in the presence of alkyl alcohols.[2]

Reaction Products.—BF and BFA were almost exclusive products from thermal decomposition at 80 °C of DDM (0.05M) in oxygen-saturated anhydrous chlorobenzene. When the reaction was carried out in the presence of equimolar amounts of the sulphur compounds (5)—(8) TFE was the major product and small amounts of DBE were also observed. In such conditions the yield of BF and BFA was found to be remarkably reduced. Added water brought about the formation of larger amounts of DBE at the expense of TFE. The product distribution from the decomposition at 80 °C of DDM both in the absence and in the presence of equimolar amounts of sulphur compounds (5)—(8) is reported in Table 4.

TABLE 4

Product ratios obtained from thermal decomposition at 80 °C of DDM (0.05M) in chlorobenzene solution carried out under oxygen in the presence of sulphur compounds (0.05M)

	Product ratios (%) [a]			
Sulphide	BF	BFA	TFE	DBE
None	70	30	n.d.	n.d.
BTD	34	14	50	5
TL	32	11	52	5
BFS	28	13	54	5
DBS	31 (33) [b]	13 (12)	53 (29)	3 (26)

[a] Overall yields, calculated on starting DDM, amounted to *ca.* 90—95%. [b] Figures in parentheses refer to a reaction carried out in commercial chlorobenzene, containing *ca.* 0.1% water.

The product proportions are also influenced by the concentration of the sulphide present, as evidenced in Table 5, which shows the effect of changing BTD concentration on product distribution. A progressive increase in TFE (and concomitant reduction in the yield of BF) results as the concentration of BTD increases; however the yield of BFA remains roughly constant over the range of BTD concentrations investigated.

TABLE 5

Product ratios obtained from thermal decomposition at 80 °C of DDM (0.05M) in chlorobenzene solution carried out under oxygen in the presence of BTD

	Product ratios (%) [a]			
[BTD]/M	BF	BFA	TFE	DBE
0.005	45 (47) [b]	11 (12)	42 (29)	2 (12)
0.05	34	14	50	2
0.20	21	13	60	6

[a] Overall yields were *ca.* 90—95%. [b] Figures in parentheses refer to a reaction carried out in commercial chlorobenzene, containing *ca.* 0.1% water.

Thermal decomposition at 80 °C of DDM in oxygen-saturated chlorobenzene containing n-butanol (0.1—10M) produced diphenylmethyl n-butyl ether (BBE), diphenylmethane (DFM), BF, and BFA. Yields of BBE and DFM were found to increase at the expense of benzophenone with increasing concentration of n-butanol, the BBE/DFM ratios remaining roughly constant throughout the range of n-butanol concentrations. These findings are in agreement with a previous report[3] of the thermal decomposition of DDM at 85 °C in oxygen-saturated acetonitrile in the presence of isopropyl alcohol, in which case the observed constancy of the ratio diphenylmethyl isopropyl ether/diphenylmethane was explained in terms of competitive reaction of diphenylcarbene singlet and triplet with the alcohol. Parallel reactions carried out in chlorobenzene–n-butanol mixtures in the presence of dibenzyl sulphide (0.005M) did not lead to changes in the reaction products (apart from the presence of tetraphenylethylene in small amounts observed at an n-butanol concentration of 0.1M), but a significant variation of the product distribution was produced at an n-butanol concentration of 0.1—2.0M, in which range formation of much larger amounts of diphenylmethyl n-butyl ether was accompanied by a considerable reduction in the yield of benzophenone and diphenylmethane. At n-butanol concentrations >5.0M, however, the yield of diphenylmethyl n-butyl ether, benzophenone, and diphenylmethane was found to be unaffected by the presence of dibenzyl sulphide. Product proportions obtained from decomposition of DDM in chlorobenzene/n-butanol mixtures are collected in Table 6 and the corresponding BBE/DFM and BF/DFM ratios in Table 7.

TABLE 6

Product ratios obtained from thermal decomposition at 80 °C of DDM (0.05M) in chlorobenzene–n-butanol mixtures under oxygen (A) and under oxygen in the presence of DBS (0.005M) (B)

	Product ratios (%) [a]						
	A			B			
[BuOH]/M	BF	BBE	DFM	BF	BBE	DFM	TFE
0.1	57	40.0	3.0	13	83.0	n.d.	4
0.2	56	40.0	4.0	13	87.0	$\sim$0.2	n.d.
0.5	47	48.5	4.5	8	92.0	$\sim$0.2	n.d.
1.0	35	60.0	5.0	10	89.0	1.0	n.d.
2.0	25	69.5	5.5	8	90.7	1.3	n.d.
5.0	16	77.0	7.0	16	79.0	5.0	n.d.
10.0	16	77.0	7.0	16	77.0	7.0	n.d.

[a] Overall yields were *ca.* 85—90%. BFA was also formed in *ca.* 5—10% yields.

TABLE 7

BBE/DFM and BF/DFM ratios for thermal decomposition of DDM (0.05M) at 80 °C in chlorobenzene–n-butanol mixtures in the presence of oxygen and DBS (0.005M)

[BuOH]/M	BBE/DFM ratios [a]	BF/DFM ratios [a]
0.1	n.d. (14)	n.d. (19)
0.2	$\sim$500 (10)	$\sim$60 (14)
0.5	$\sim$500 (11)	$\sim$40 (10)
1.0	100 (12)	10 (7)
2.0	70 (12)	6 (4.5)
5.0	16 (11)	3.2 (2.3)
10.0	11 (11)	2.3 (2.3)

[a] Figures in parentheses refer to reactions carried out in the absence of DBS.

DISCUSSION

Kinetic and product results suggest that in the thermal decomposition at 80° of DDM in oxygen-saturated chlorobenzene in the presence of the sulphur compounds (5)—(8) chain decomposition of DDM can be induced by some species acting as initiator in competition with a mechanism leading to formation of diphenylcarbenes. The occurrence of this chain decomposition mechanism is dependent on the concentration and the nature of the sulphide present and it can become very significant (if not exclusive) according to the reaction conditions employed. The nature of the reaction products observed in the decomposition of DDM carried out in chlorobenzene and chlorobenzene–n-butanol suggests that the chain carrier should be the diazoalkane radical cation, $Ph_2CN_2^{+\cdot}$.

The reaction of the chain carrier with a DDM molecule and loss of nitrogen would afford tetraphenylethylene radical cation and then TFE by extraction of an electron from a further molecule of DDM.[4] The formation of bisdiphenylmethyl ether could be accounted for by reaction of the chain carrier with traces of water still present in nominally anhydrous chlorobenzene, as evidenced by experiments using commerical chlorobenzene containing *ca.* 0.1% water which clearly showed an increase in the yield of bisdiphenylmethyl ether at the expense of the yield of tetraphenylethylene. We assume that DBE might arise from attack of water on the chain carrier to give $(Ph_2COH_2)^{+\cdot}$ from which a 1,2-hydrogen shift and subsequent attack on a diazoalkane molecule would afford bisdiphenylmethyl ether radical cation and finally DBE by electron transfer from a further diazoalkane molecule.

On the other hand reaction of the chain carrier with n-butanol would give diphenylmethyl n-butyl ether through a mechanism analogous to that suggested for reaction with water.

Evidence that formation of diphenylmethyl n-butyl ether is essentially due to attack of the chain carrier (rather than diphenylcarbene) on n-butanol appears to be clearly supported from results obtained from decomposition of DDM carried out in chlorobenzene–n-butanol in the presence and in the absence of dibenzyl sulphide (6) (Table 6). In fact the considerable increase in the yield of diphenylmethyl n-butyl ether and the very remarkable increase in the BBE/DFM ratios observed in the reactions carried out in the presence of DBS indicate that, at least at n-butanol concentrations of 0.1—1.0M, formation of BBE is mostly due to reaction of n-butanol with the chain carrier rather than with diphenylcarbene. With further increasing n-butanol concentrations, progressive, and at n-butanol concentrations >5.0M, practically total, occurrence of the carbene reaction with the alcohol takes place. The kinetic evidence appears to be in line with these conclusions, as indicated by the progressive decrease in the k_{cat}/k_1 ratios at n-butanol concentrations > *ca.* 0.5M and by the fact that the rate of disappearance of diazoalkane is unaffected by the presence of DBS at n-butanol concentrations >5M. The suppression of the chain decomposition of the diazoalkane observed at the highest concentrations of n-butanol, at which the alcohol acts as a very effective trap for diphenylcarbene, could be reasonably taken as proof that diphenylcarbene should be involved in the process leading to the chain carrier.

Over the range of n-butanol concentrations investigated the suppression of tetraphenylethylene was observed, thus pointing to a preferential reaction of the chain carrier with the alcohol rather than with DDM.

As for BFA, a noticeable reduction in the yield was observed in reactions carried out in the presence of the sulphur compounds (5)—(8). These findings might lead at first sight to the conclusion that BFA is not formed essentially by reaction of the chain carrier with unchanged diazoalkane. In the reaction conditions employed, reaction between two diazoalkane molecules (and/or attack of diphenylcarbene on DDM) could be responsible for the formation of BFA. However the possible role played by attack of the chain carrier at the terminal nitrogen atom of a molecule of DDM leading to BFA radical cation and then to BFA by removal of an electron[4] cannot be readily evaluated.

The remarkable reduction in the yield of BF encountered in the decomposition of DDM in chlorobenzene solution in the presence of the sulphides (5)—(8)

suggests that BF is the product only of reaction of triplet diphenylcarbene with oxygen;[3] however another route leading to benzophenone might be opened in such conditions, as apparently evidenced by reactions carried out in chlorobenzene–n-butanol mixtures. In fact, if it is granted[3] that benzophenone and diphenylmethane are products of reaction of triplet diphenylcarbene with oxygen and n-butanol respectively, a significant increase in the BF/DFM ratio observed for reactions carried out in the presence of DBS (Table 7) might be taken as evidence that BF can also be formed through some different route. The main features of the proposed reaction pathways are indicated in Scheme 2.

Recently a chain decomposition of DDM at 30 °C induced by copper(II) perchlorate and by tris-(*p*-bromophenyl)ammoniumyl perchlorate has been reported by Bethell and his co-workers.[4] In acetonitrile TFE was formed as the major product together with minor amounts of BFA. Attack of the proposed chain carrier, *i.e.* the diazoalkane radical cation, on a diazomethane molecule has been postulated to occur in the rate-controlling process. From a study carried out in acetonitrile–water it was inferred that in the presence of water, incursion of an acid-catalysed decomposition pathway involving formation of diphenylmethyl cations occurs, most reasonably induced by proton transfer from ($Ph_2COH_2^{+\cdot}$), produced by attack of water on the diazoalkane radical cation. Moreover it was established that the acid-catalysed reaction is not significant at low water concentrations.

In our attempt to rationalize the formation of bisdiphenylmethyl ether we have above suggested intermediacy of the same radical cation as previously proposed by Bethell, *i.e.* $(Ph_2COH_2)^{+\cdot}$, produced by reaction of the chain carrier with water. In the proposed reaction pathway leading to bisdiphenylmethyl ether we have assumed that such a radical cation should undergo a preferential 1,2-hydrogen shift rather than intermolecular proton transfer as suggested by Bethell, since the proton transfer mechanism does not appear to open a readily explainable route to the formation of bisdiphenylmethyl ether. Our assumption also rests on the fact that no diphenylmethanol could be detected in our reactions, whereas formation of diphenylmethanol (and not of bisdiphenylmethyl ether) was observed by Bethell even at very low water concentrations; the different behaviour apparently exhibited by $(Ph_2COH)^{+\cdot}$ might be well ascribed to the significant difference in reaction conditions.

As for reactions carried out in chlorobenzene–n-butanol it might be assumed, in analogy with the suggestion for the reaction with water, that a 1,2-hydrogen shift is the preferred reaction path undergone by the radical cation produced by attack of n-butanol on the chain carrier, at least at low concentrations (0.1—0.2M). Supporting evidence comes from our findings that TFE was only formed in very small yields (or not formed at all) in such conditions, whereas noticeable formation of TFE would be expected if proton transfer (and thus acid-catalysed decomposition of DDM) should play a significant role.[5] At higher n-butanol concentrations some incursion of a proton transfer mechanism would possibly be expected to be more likely, but it is not supported by any definite evidence at this time. In fact the increase in the rate of disappearance of DDM observed for n-butanol concentrations in the range 0.2—0.5M might be consistent either with a facilitating effect exerted by the alcohol in the propagation of the radical-cation chain or with a significant incursion of an acid-catalysed decomposition mechanism. It should be noted that our kinetic and product results could be reasonably rationalized by assuming the intervention as chain carrier of either the diazoalkane radical cation or the corresponding carbene radical, $Ph_2C^{+\cdot}$, which might derive from $Ph_2CN_2^{+\cdot}$ by unimolecular nitrogen loss. In the chain decomposition of DDM induced by copper(II) and ammoniumyl salts, kinetic evidence allowed the exclusion of the possibility that the chain carrier could be the carbene radical, but this cannot be ruled out in our case.

Finally we point out that we can give no convincing explanation of the process leading to the initiation of the chain decomposition of DDM observed in our conditions. The kinetic evidence, indicating a progressive increase in the concentration of chain initiator during the reaction, as well as our observation that diphenylcarbene is likely to be involved in the initiation process would suggest unimolecular decomposition of DDM to be the rate-controlling step in the formation of the chain initiator; however the question of the role played by diphenylcarbene in conjunction with oxygen and sulphides (5)—(8) in the process responsible for the formation of the chain initiator is still open and requires further studies.

EXPERIMENTAL

Diazodiphenylmethane,[6] benzophenone azine,[7] bisdiphenylmethyl ether,[8] diphenylmethyl n-butyl ether,[9] 1,2,3-benzothiadiazole (8),[10] dibenzyl sulphide (5),[11] and benzyl phenyl sulphide (6)[12] were prepared according to the literature. Benzophenone, tetraphenylethylene, and thiolan (7) were commercial products.

Kinetic Measurements.—Solutions for kinetic determinations were prepared by mixing aliquot parts of chlorobenzene solutions of diazoalkane, sulphur compound, and n-butanol. Reactions were carried out in Pyrex vessels at 80 ± 0.1 °C; oxygen was gently bubbled into the previously oxygen-saturated mixtures during kinetic determinations. Portions were removed at regular intervals, suitably diluted with chlorobenzene and assayed by measuring the area of the diazo band in the i.r. spectrum at *ca.* 2 040 cm^{-1}. The first portion was removed after 5 min from immersion of the reaction vessel in the thermostatted bath and taken as zero point.

Product Analysis.—All the products were identified by spectral comparison with authentic specimens after separation by column chromatography. Quantitative analyses were performed by g.l.c. on a Varian 1440 instrument, using a 5% SP 2250 on Supelcoport column, with the internal standard method.

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