Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part X.[1] Kinetic and Mechanistic Studies of the Decomposition of Diphenyldiazomethane catalysed by Copper(II) Bromide

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The kinetics and products of decomposition of diphenyldiazomethane catalysed by copper(II) bromide in acetonitrile have been investigated. It is shown that the catalyst solution reacts rapidly with an equivalent of the diazoalkane in a rapid two-step process, stage (i), yielding a copper complex which may have diphenylmethylene as a ligand. Stopped-flow measurements on the kinetics of this reaction are described. The copper complex formed in stage (i) then consumes the excess of diazoalkane in a much slower stage (ii). The effects of the initial diazoalkane and catalyst concentrations and of added lithium bromide on the rate and kinetic form of this stage lead to the proposal of a reaction scheme involving three main pathways, one leading to benzophenone and two to benzophenone azine. Using this proposed scheme, it is shown that both initial rates of disappearance of diphenyldiazomethane and the final product proportions can be approximately predicted under most reaction conditions. During this stage of the reaction, some 10% of the catalyst is precipitated as an unstable paramagnetic complex. After all the diazoalkane has been consumed, this precipitate slowly redissolves, and the original catalyst solution is regenerated.

COPPER compounds and metallic copper have long been known to bring about the decomposition of diazo-alkanes.[2] In some cases, diazomethane for example, loss of nitrogen leads to polymers, but more commonly products are formed which appear to have arisen from intermediate carbenes. Thus, in the presence of olefins, cyclopropanes are formed. However, differences in products between copper catalysed and photochemical decompositions of the same diazoalkane, for example the absence of C–H insertion products under the former conditions, have led to the view, first clearly expressed by Yates,[3] that the reactive intermediate in the presence of copper is a complexed carbene (carbenoid) rather than the free divalent carbon species. Unequivocal support for the importance of carbene-copper complexes in the product-determining stages of reaction has come from observations that a chiral copper(II) complex promotes the decomposition of ethyl diazoacetate in the presence of styrene giving cyclopropanes which are optically active,[4] and that copper(I) halide-trialkyl phosphite complexes promote cyclopropane formation with stereoselectivity determined by the nature of the alkyl groups of the phosphite.[5]

Direct observation of the kinetics of the decomposition of diazoalkanes catalysed by copper compounds in homogeneous solution has not previously been reported. Following our interest in this area,[1] we undertook a kinetic study of the homogeneous reaction of diphenyl-diazomethane with copper(I) and copper(II) compounds in acetonitrile. Our aim was to gain further insight into the mechanism of catalysis and the nature of the intermediate complexes. In this paper we describe our observations and offer a tentative mechanistic interpretation of the reaction of diphenyldiazomethane with copper(II) bromide.

RESULTS

General Features of the Reaction.—In order to facilitate comparison with our earlier work, the solvent used in this investigation was acetonitrile and, as used, it contained typically 0·01% residual water. Solutions of copper(II) bromide in this solvent are green ($\lambda_{max.}$ 640 mm), the colour being attributed to a charge-transfer transition of the anion $CuBr_3^-$ or its dimer[6] (but see below).

Addition of excess of diphenyldiazomethane to acetonitrile solutions of copper(II) bromide causes immediate evolution of nitrogen and the solution takes on a brown colour [$\lambda_{max.}$ 526 (due to the diazo-compound) and 690 nm]. This colour fades at a conveniently measurable rate, and a small amount of a dark green, gelatinous material separates. When all the diphenyldiazomethane has decomposed, the supernatant liquid appears colourless, but, on standing, the precipitate dissolves and the solution takes on again its original green colour. Analysis of the reaction mixture

[1] Part IX, D. Bethell and K. C. Brown, *J.C.S. Perkin II*, 1972, 895.

[2] For reviews see (a) E. Müller, H. Kessler, and B. Zech, *Fortschr. Chem. Forsch.*, 1966, **7**, 125; (b) G. W. Cowell and A. Ledwith, *Quart. Rev.*, 1970, **24**, 119; (c) D. Bethell, *Adv. Phys. Org. Chem.*, 1969, **7**, 153; (d) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[3] P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 5376.

[4] M. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, 1968, **24**, 3655.

[5] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

[6] W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, 1963, **46**, 1848; J. C. Barnes and D. N. Hume, *Inorg. Chem.*, 1963, **2**, 444.

after completion of the reaction shows that the diazoalkane is transformed into benzophenone and benzophenone azine, together with a small amount of tetraphenylethylene. These are the same products as are formed on thermal [7] or zinc halide catalysed [1] decompositions of diphenyldiazomethane in acetonitrile. The proportion of ketone may be increased by using more aqueous acetonitrile as solvent and decreased somewhat by carrying out the reaction under nitrogen.

The overall reaction evidently consists of three main stages, (i) a rapid reaction of the components of the original solution of copper(II) bromide in acetonitrile with the diazo-compound, (ii) a much slower consumption of the diazo-compound remaining after the first stage, and (iii) regeneration of the catalyst solution. Each stage will be described in turn.

Stage (i).—*Stoicheiometry.* The initial reaction of diphenyldiazomethane with the copper(II) bromide solution takes place very rapidly. The stoicheiometry of the process can be established by extrapolating the diazoalkane concentration–time curve of the subsequent decomposition, followed spectroscopically in the i.r. region or by nitrogen evolution, to zero time (see Figure). The results indicate that one diphenyldiazomethane molecule is consumed with loss of one molecule of nitrogen for each atom of copper present.*

Confirmation that nitrogen is lost in the initial reaction and that diazoalkane is not bound as such to copper comes from quenching experiments using cyanide ion. Addition of a drop of a saturated, aqueous solution of potassium cyanide to a portion (2 ml) of a reaction mixture (initially $[Ph_2CN_2] = 1.0 \times 10^{-2}M$, $[CuBr_2] = 1.99 \times 10^{-3}M$) precipitates all the copper as copper cyanide and thus stops the reaction. The results in Table 1 show that the amount of diazoalkane recoverable after quenching is the same as that detectable spectrophotometrically in the reaction mixture at the same time. Clearly no additional diazoalkane is released when cyanide replaces the copper ligands.

Kinetics. Although rapid, the kinetics of the initial reaction of diphenyldiazomethane and the copper(II) bromide solution can be followed by monitoring the disappearance of the absorption at 640 nm using the stopped-flow technique. The optical density of copper(II) bromide solutions at this wavelength is directly proportional to the total copper concentration, an observation which incidentally makes it unlikely that the ion $CuBr_3^-$ and its dimer both contribute to the absorbance.

The shape of the decay curves indicates a fairly rapid initial decrease in optical density to *ca.* 10—20% of the initial value, followed by a very much slower disappearance of the residual absorption. By linear extrapolation of the slower portion to zero time and subtraction of the extrapolated optical densities from the total absorbance, the initial rapid disappearance of the green colour was found to obey a first-order kinetic law over several half-lives provided that diphenyldiazomethane was in large excess (> fourfold) over the concentration of copper(II) bromide. The kinetic results are in Table 2. We presume that the subsequent slow decay of absorption at 640 nm represents the consumption of another intermediate (again, perhaps that having its maximum absorption at 690 nm).

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* By extrapolating to zero the curves of optical density at 526 nm against time, the stoicheiometry appears to be copper : diphenyldiazomethane 2 : 1; presumably an intermediate, perhaps the one responsible for the peak at 690 nm, contributes to the absorption at 526 nm.

The results in Table 2 indicate that the rate of disappearance of the 640 nm absorption is not directly proportional to the concentration of diphenyldiazomethane in the reaction mixture. The rate coefficients reach a maximum value at fairly low diazoalkane concentrations as expected
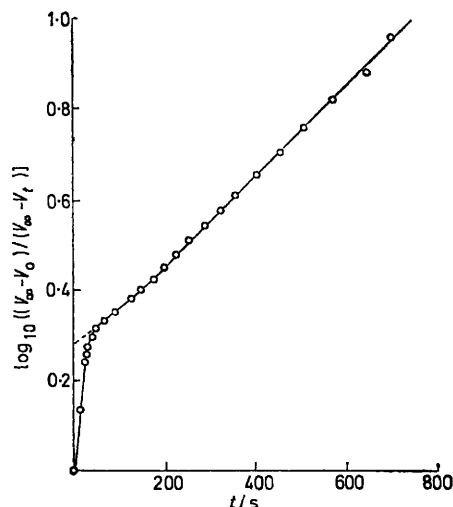
Kinetics of nitrogen evolution from the reaction of Ph_2CN_2 ($2.66 \times 10^{-2}M$) and $CuBr_2$ ($8.7 \times 10^{-3}M$) in acetonitrile at $21.4°$. The intercept at $t = 0$ corresponds to the evolution of 30.3% of the available nitrogen

TABLE 1

Concentrations of diphenyldiazomethane extractable from reaction mixtures containing copper(II) bromide after treatment with potassium cyanide at 30°

$[CuBr_2]_i = 1.99 \times 10^{-3}M$

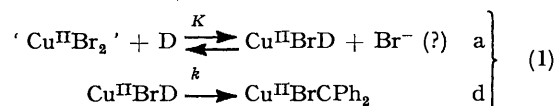|	$10^3[Ph_2CN_2](M)$	
Reaction time (s)	KCN	Control
0		9.4 [a]
25	7.3	7.4
300	5.3	5.4

[a] Before addition of copper(II) bromide.

TABLE 2

First-order rate coefficients (k_{obs}) for the initial decrease in absorbance at 640 nm in solutions of copper(II) bromide and diphenyldiazomethane in acetonitrile solution at 30° by the stopped-flow method

$[CuBr]_i = 9.95 \times 10^{-4}M$

$10^3[Ph_2CN_2]_i(M)$	1.38	1.89	3.98	7.15	9.47
$k_{obs}(s^{-1})$ [a]	5 [b]	8 [b]	11	14	13

[a] Estimated uncertainty ± 1 s[1]. [b] From initial linear portions of first-order kinetic plots.

for a reaction scheme involving a pre-equilibrium [equation (1); ' $Cu^{II}Br_2$ ' represents all the reactive copper(II) species,

$$' Cu^{II}Br_2 ' + D \underset{k}{\overset{K}{\rightleftharpoons}} Cu^{II}BrD + Br^- (?) \quad a$$
$$Cu^{II}BrD \xrightarrow{k} Cu^{II}BrCPh_2 \quad d$$
$$\left. \right\} \quad (1)$$

complete with ligands, originally present in solution, $Cu^{II}BrD$ a complex derived by interaction of them with the diazoalkane D without loss of nitrogen, and $Cu^{II}BrCPh_2$ is the final product of this stage after nitrogen is lost]. The

[7] D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 1965, 2466; D. Bethell, A. R. Newall, G. Stevens, and D. Whittaker, *J. Chem. Soc.* (*B*), 1969, 749.

expression for the observed first-order rate coefficients for the disappearance of the absorption at 640 nm is then given by equation (2). The number and precision of our results

$$k_{\mathrm{obs}} = kK[\mathrm{Ph_2CN_2}]/([\mathrm{Br^-}] + K[\mathrm{Ph_2CN_2}]) \qquad (2)$$

does not justify a more detailed quantitative treatment, although the value of K must be of the order of 10^3 l mol^{-1}.

Stage (ii).—*Kinetics.* The slow stage during which most of the diphenyldiazomethane is normally consumed can be followed by a variety of techniques. Nitrogen evolution and spectrophotometry at 526 or 690 nm or in the i.r. at 2040 cm^{-1} have all been examined.

The evolution of nitrogen is not simply related to the progress of the reaction. The azine which is produced retains half the nitrogen of the diazoalkane from which it is formed while benzophenone and tetraphenylethylene retain none. Moreover, the proportions in which the azine and ketone are formed depend upon the diazoalkane concentration (see below). Consequently, only in the late stages of reaction, when the diazoalkane concentration is low and the product formed is largely benzophenone, does the rate of production of nitrogen accurately parallel the disappearance of diphenyldiazomethane. The reaction then obeys a simple first-order kinetic law and the derived rate coefficients agree with values obtained by other techniques. One of our experiments is illustrated in the Figure.

The disappearance of the absorption due to diphenyldiazomethane at 526 nm can be used to follow the reaction. However, as indicated above, some interference from other absorbing species occurs and the technique was not used extensively. Changes in absorbance at 690 nm were also monitored in some experiments. At initial copper(II) bromide concentrations $>5 \times 10^{-3}$M, the absorbance at this wavelength fell continuously with a half-life close to that for the disappearance of the excess of diazoalkane. At a lower concentration of copper(II) bromide, the absorbance at 690 nm increased during the first 8 min of reaction but fell again thereafter.

The usual method of following the disappearance of diphenyldiazomethane was by i.r. spectroscopy using the intense absorption of the diazo-function at 2040 cm^{-1}. Up to diazoalkane concentrations of 1.5×10^{-2}M Beer's law applies but at higher concentrations the measured density falls progressively below the value predicted on the basis of simple proportionality. Almost all experiments were conducted under conditions where the free diazoalkane concentration was $<1.5 \times 10^{-2}$M.

Kinetic experiments fall into four categories, (a) experiments in which the initial diazoalkane concentration was roughly constant and the copper(II) bromide concentration varied, (b) experiments in which the initial diazoalkane concentration exceeded the catalyst concentration by a constant amount, (c) experiments similar to those in (a) but in which lithium bromide was present in large excess, and (d) experiments as in (c) but in which lithium bromide was present at four times the catalyst concentration.*

The kinetic form of the disappearance of the diazoalkane showed some unusual features. At low catalyst concentrations (10—20% of the initial diazoalkane concentration) and in the absence of added lithium bromide the disappearance followed a first-order kinetic law over several half-lives. However, at higher catalyst concentrations,

* Control experiments confirmed that lithium bromide alone does not cause decomposition of diphenyldiazomethane under these conditions.[8]

when the diazoalkane concentration at the beginning of stage (ii) was therefore low, first-order kinetic plots showed downward curvature in the later stages indicating a kinetic order between 0 and 1. Clean zeroth-order kinetics could be observed under these conditions if large concentrations of lithium bromide were added. The kinetic results are therefore recorded in Tables 3—5 as initial rates to facilitate comparison and also to avoid complications arising from the formation of the precipitate. These initial rates were obtained graphically from plots of optical density against time and values could be reproduced within 10%.

TABLE 3

Initial rates of decomposition of diphenyldiazomethane catalysed by copper(II) bromide in acetonitrile solution at 30°

$10^3[\mathrm{CuBr_2}]_i$(M)	$10^2[\mathrm{Ph_2CN_2}]_i$(M)	$10^6 v_0$ (mol l^{-1} s^{-1})	Complex ratio $\mathrm{Ph_2CN_2 : CuBr_2}$
0·53	0·87	2·7	1·21
1·08	1·00	4·7	0·87
2·15	1·00	7·0	0·99
3·05	1·08	10·1	1·38
4·50	0·97	13·1	1·13
4·99	0·94	12·8	0·90
6·11	1·00	12·5	1·03
6·95	0·97	14·3	1·07
8·08	0·97	18·0	0·88

TABLE 4

Initial rates of decomposition of diphenyldiazomethane, at constant initial concentration ($[\mathrm{Ph_2CN_2}]_0$), catalysed by copper(II) bromide in acetonitrile solution at 30°

$10^3[\mathrm{CuBr_2}]_i$(M)	$10^2[\mathrm{Ph_2CN_2}]_i$(M)	$10^6 v_0$ (mol l^{-1} s^{-1})	Complex ratio $\mathrm{Ph_2CN_2 : CuBr_2}$
0·9	1·09	4·9	0·98
1·0	1·10	6·1	1·59
2·0	1·20	9·1	1·60
3·1	1·31	15·4	1·22
4·0	1·40	21	1·38
6·0	1·60	36	1·08
8·0	1·80	47	1·25
10·0	2·00	50	0·92

TABLE 5

Influence of added lithium bromide on the kinetics of the decomposition of diphenyldiazomethane catalysed by copper(II) bromide in acetonitrile solution at 30°

$10^3[\mathrm{CuBr_2}]_i$ (M)	$10^2[\mathrm{Ph_2CN_2}]_i$ (M)	Kinetic order [a] in $\mathrm{Ph_2CN_2}$	$10^6 v_0$ (mol l^{-1} s^{-1})
(a) [LiBr] : [CuBr₂]ᵢ 4·0			
1·91	1·0	1	1·6
3·82	1·0	1	6·0
4·80	1·0	1	7·6
6·10	1·0	1	7·7
7·65	1·0	0—1	7·2
(b) [LiBr] 8·9 × 10⁻²M			
1·0	1·0	0—1	2·5
2·0	1·0	0—1	3·6
4·0	1·0	0—1	6·1
6·0	1·0	0	8·1
8·0	1·0	0	9·3

It is clear from the results that the initial reaction rate is related to the catalyst concentration in a rather complex way. In some instances increasing the catalyst concentration actually reduces the rate of disappearance of the diazoalkane. Comparison of the results in Tables 3 and 4 makes it clear, however, that increasing the diazoalkane

[8] S. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, 1969, **34**, 25.

concentration at a fixed concentration of copper(II) bromide generally increases the initial rate as expected on the basis of observations during individual kinetic runs. At a fixed diazoalkane concentration the initial rate shows a direct proportionality to the catalyst concentration. Most revealing, however, are the effects of the addition of lithium bromide. Compared with runs in its absence, addition of lithium bromide causes a decrease in the initial reaction rate. On the other hand, large concentrations of lithium bromide cause rate increases compared with reactions at lower concentrations. It seems clear therefore that the added bromide ion has the ability to inhibit one reaction pathway at low concentrations, but to facilitate another reaction pathway at high concentrations. Moreover, since high concentrations of bromide ion favour zeroth-order kinetics in diazoalkane, it would seem that this reaction is one between bromide ion and the copper-containing species resulting from stage (i). We shall return to these points in the Discussion section.

Precipitate formation. During the course of stage (ii) a dark green, gelatinous precipitate separated. Isolation by centrifugation followed by washing with acetonitrile and drying under nitrogen yielded a microcrystalline solid. Analytical figures from different preparations varied a little, but typical figures are Cu, 40; Br, 25; C, 7; H, 3%. Typically, some 10% of the available copper was converted into this precipitate. The organic material suggested by the presence of carbon could be released on treatment of the precipitate with dilute aqueous hydrochloric acid. Benzophenone and its hydrazone were both detectable by t.l.c. Since benzophenone hydrazone is hydrolysed at an appreciable rate under the conditions of the decomposition of the precipitate, it could well be that only this compound is liberated by the acid.[9] On this basis, *ca.* 9% of the precipitate is benzophenone hydrazone or a precursor.

The precipitate yielded a reflectance spectrum consisting of a broad peak at 830 nm and a further peak at 270 nm with a shoulder at 360 nm. The most notable feature in the i.r. spectrum was a strong absorption at 3410 cm^{-1}. The material is paramagnetic with a suceptibility measured on a Faraday balance of 7.57×10^{-6} c.g.s. units.

Decomposition occurred on exposure of the isolated precipitate to the atmosphere or on treatment of the precipitate suspended in acetonitrile with water. A pale green, insoluble product was formed having an i.r. spectrum very similar to that of basic copper bromide $CuBr_2,3Cu(OH)_2$.

The precipitate slowly decomposed diphenyldiazomethane over a period of several hours, much too slow to complicate the observed kinetics of diazoalkane disappearance under normal conditions. Moreover, the precipitate was not consumed in the control experiment whereas under normal conditions it dissolves as the initial green colouration is restored. This dissolution clearly bears no relation to the hydrolysis of the precipitate described above; reaction with another component of the reaction mixture is indicated.

Stage (iii).—When all the free diazoalkane had disappeared reaction solutions appear colourless. Over the next 1—2 h the original green colour of the solution reappears, the increase in absorbance at 640 nm following an S-shaped curve, as the precipitate dissolves. The rate of this stage of the reaction was essentially unaffected by bubbling dry oxygen through the mixture. However, in an

[9] *Cf.* M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Comm.*, 1967, 1106; P. E. Baikie and O. S. Mills, *ibid.*, p. 1228.

experiment conducted entirely under nitrogen, the colour of the solution after consumption of all the diphenyldiazomethane was pale green, no precipitate was formed, and there was no restoration of the 640 nm absorption.

Products.—Under the conditions of the present reactions, the only identifiable products were benzophenone, benzophenone azine, and a little tetraphenylethylene. Chlorine-containing products have been identified in the reactions of diphenyldiazomethane with copper(II) chloride in acetonitrile.[10] However, it should be borne in mind that sufficient water was present in our reaction mixtures to hydrolyse for example dibromodiphenylmethane completely in concentrations up to that of the original diazoalkane. Indeed the proportion of benzophenone in the reaction mixture could be increased by the addition of water. On the other hand, the proportion of benzophenone could be decreased a little by carrying out the reaction in an apparatus from which oxygen had been removed by several freeze–pump–thaw cycles. Exclusion of oxygen had no detectable effect on the rate of disappearance of the diphenyldiazomethane.

Product analysis was achieved by isolation, t.l.c., and, most often, by g.l.c. Results are given in Table 6. By

TABLE 6

Products formed in the decomposition of diphenyldiazomethane catalysed by copper(II) bromide in acetonitrile solution at 30°

$$[Ph_2CN_2]_i = 1.0 \times 10^{-2}M$$

$10^3[CuBr]_i$ (M)	$10^3[LiBr]_i$ (M)	Products (%) [a]		
		$Ph_2C{:}N{\cdot}N{:}CPh_2$	$Ph_2C{:}O$	$Ph_2C{:}CPh_2$
0.99		85 (89)	10 (11)	1
1.00	89	36 (32)	63 (68)	d
1.91	7.6	44 (73)	48 (27)	1.2
2.02		60 (76)	33 (24)	1
2.02 b		80	9	1
2.02 c		86 (94)	16 (6.4)	0.7
3.10		65 (67)	33 (33)	1
3.20	12.8	18 (55)	75 (45)	0.4
3.93		43 (58)	50 (42)	2
4.00	89	20 (16)	71 (84)	d
4.99		33 (47)	57 (53)	1.5
6.00	89	10 (8)	84 (92)	d
6.02		20 (36)	74 (64)	1
7.65	30.6	5.4 (8)	89 (92)	0.3
8.00		10 (16)	89 (84)	1
8.00	89	5.5 (2)	84 (98)	d

[a] Diazoalkane (%) converted into each product. The figures in parentheses are calculated using equation (10). [b] Oxygen excluded. [c] $[Ph_2CN_2]_i = 4.0 \times 10^{-2}M$. [d] Not determined.

comparison of the product yields immediately after consumption of all the free diazoalkane with those found after regeneration of the absorption at 640 nm, it was found that only benzophenone was produced during stage (iii). It would seem therefore that benzophenone in a concentration equal to that of the catalyst is produced independently of the main competitive processes occurring during the slow disappearance of the diazoalkane.

Of the three isolable products, the proportion of tetraphenylethylene is small and shows little change with changing reactant concentration; it will not be discussed further. The ketone and azine yields on the other hand change markedly when either the initial diazoalkane concentration or the copper(II) bromide concentration changes, even after allowance has been made for the ketone

[10] T. Saegusa, Y. Ito, T. Shimizu, and S. Kobayashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3535.

produced during stage (iii). Thus the azine yield decreases continuously from *ca.* 100% at low catalyst concentrations (*ca.* 10^{-3}M) to a value approaching zero as the copper(II) bromide concentration rises to that of the diazoalkane. Increasing the initial concentration of diphenyldiazomethane at a fixed catalyst level causes an increase in the proportion of azine; this is the behaviour expected in situations where an intermediate is partitioned between reaction with diazoalkane giving azine and reaction not involving diazoalkane giving ketone.[7] Addition of lithium bromide has the effect of increasing the proportion of ketone in the final product mixture.

DISCUSSION

The foregoing account of the decomposition of diphenyldiazomethane by copper(II) bromide in acetonitrile demonstrates the complexity of the reaction. The mechanistic inferences which we draw are therefore necessarily tentative, although the agreement which we have been able to achieve between experiment and the predictions of our mechanism makes us hopeful that these conclusions are useful. We shall focus attention particularly on stage (ii) of the reaction in which a copper-containing species produced in stage (i) reacts with diphenyldiazomethane.

An important question concerns the oxidation state of copper in the species responsible for the reaction in stage (ii). We have no direct observations which enables us to answer this question, but indirect evidence suggests that the metal may be present as copper(II). First, copper(I) bromide causes decomposition of the diazoalkane but does not form appreciable concentrations of complex as occurs in stage (i) of the reaction. Secondly, transient absorption at *ca.* 690 nm appears during stage (ii) and this can occur in copper(II) but not in copper(I) complexes. However, after all the excess of diazoalkane has been consumed, the reaction mixture shows no visible absorption. Thirdly, the material precipitated during stage (ii) is paramagnetic and hence contains copper in the +2 oxidation state. It should be noted that the oxidation potential of diphenyldiazomethane [11] and the reduction potential of copper(II) ion [12] are estimated to be virtually identical in acetonitrile.

As indicated earlier the kinetic dependence of the reaction is 0—1 in diphenyldiazomethane and approximates to 1 in catalyst under certain conditions. Added lithium bromide has a dual effect, reducing the rate of reaction at one concentration but, on increasing the concentration, causing some rate increase. It would seem therefore that bromide ion first inhibits a rather rapid reaction of the copper-containing species from stage (i) with diazoalkane, but, when this is virtually wholly suppressed, enhances the rate of another rather slower reaction of the copper compound presumably by direct reaction since zeroth-order kinetics in diazoalkane become dominant. On the basis of such arguments, we

[11] W. Jugelt and F. Pragst, *Angew. Chem.*, 1968, **80**, 280; *Tetrahedron*, 1968, **24**, 5123.

therefore propose the reaction pathways shown in the Scheme as an outline of the mechanism of decomposition. The features to note are as follows: (*a*) the copper-containing complex produced in stage (i) contains a bromine atom and the elements of diphenylmethylene, probably present as separate ligands although a $CBrPh_2$

SCHEME
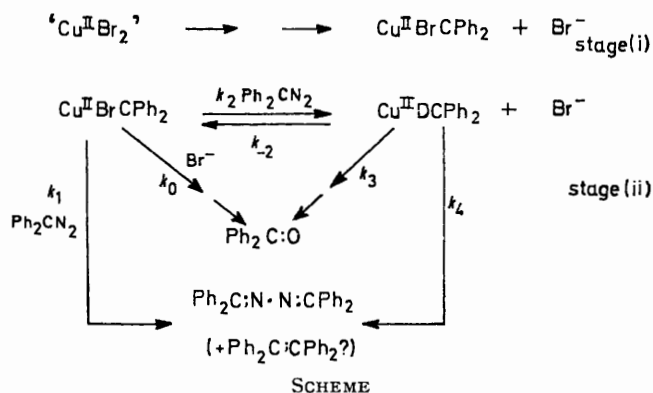
ligand cannot be completely ruled out; other ligands are omitted for simplicity; (*b*) the residual bromo-ligand can be reversibly displaced by a diazoalkane molecule; (*c*) the resultant reactive complex can collapse yielding azine and perhaps also ketone, although the detailed pathway to the latter product is not clear (*cf.* ref. 1). Competing with this pathway are reactions of the initial complex with diphenyldiazomethane directly yielding azine and with bromide ion yielding dibromodiphenylmethane which would hydrolyse in the reaction medium to give benzophenone. Since the function of the copper bromide is catalytic, product formation must result in the generation of a copper-containing species which can react rapidly with diphenyldiazomethane and hence begin a further cycle of reactions.

Using the symbolism in the Scheme, the rate of disappearance of diazoalkane is given by equation (3), where $[Cu^{II}Br_2]_i$ refers to the nominal concentration of copper(II) bromide. It can be seen that equation (3)

$$\frac{-d[Ph_2CN_2]}{dt} = [Cu^{II}Br_2]_i \left\{ k_0[Br^-] + \right.$$
$$\left. k_1[Ph_2CN_2] + \frac{k_2[Ph_2CN_2](k_3 + k_4)}{k_{-2}[Br^-] + k_3 + k_4} \right\} \quad (3)$$

contains both zeroth- and first-order terms in diazoalkane and, because of the relation of $[Br^-]$ to the catalyst concentration through our assumption that bromide ion is displaced in stage (i), a rather complex dependence on the initial concentration of copper(II) bromide. We have attempted to use an equation of the form of (3) to reproduce our observed initial rates of disappearance of diphenyldiazomethane by inserting values for the rate coefficients. No attempt has been made to optimise the fit, but rather we have looked for reproduction of the general form of the results.

[12] I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, 1957, **79**, 1852.

Equation (4) is the relation which we have used, and the results are shown in Table 7. It should be noted that

$$-\left\{\frac{d[Ph_2CN_2]}{dt}\right\}_{t=0} = [Cu^{II}Br_2]_i \left\{0{\cdot}01[Br^-] + \right.$$

$$\left. 0{\cdot}05[Ph_2CN_2] + \frac{0{\cdot}8[Ph_2CN_2]}{100[Br^-]+1}\right\} \quad (4)$$

the diazoalkane concentration is that at the commencement of stage (ii), that is to say after removal of an

gested (see, for example, ref, 10). The other discrepancy is in an experiment in which a catalyst : lithium bromide ratio of 1 : 4 was used where, at the lowest copper bromide concentration, the observed rate is very much lower than predicted [Table 7(c)].

The acceptability of our interpretation can be further tested by comparing the predicted and observed product distributions. The predicted ratio of azine to ketone will of course be dependent in part on the partitioning of $Cu^{II}DCPh_2$, i.e., the relative magnitudes of k_3 and k_4.

TABLE 7

Calculated initial rates for stage (ii) using equation (4)

			$10^6 \, v_0$ (mol l^{-1} s^{-1})				
$10^3[CuBr_2]_i$(M)	$10^3[Ph_2CN_2]_0$(M)	$10^3[Br^-]$(M)	Term 1	Term 2	Term 3	Total calc.	Observed
(a) From Table 3							
0·53	8·2	0·53	0·00	0·22	3·30	3·5	2·7
1·08	8·4	1·08	0·01	0·45	6·54	7·0	4·7
2·15	7·3	2·15	0·04	0·78	10·33	11·2	7·0
3·05	7·7	3·05	0·09	1·17	14·40	15·7	10·1
4·50	5·2	4·50	0·20	1·17	12·90	14·3	13·1
4·99	4·7	4·99	0·25	1·18	12·53	14·0	12·8
6·11	3·6	6·11	0·37	1·10	10·91	12·4	12·5
6·95	2·7	6·95	0·49	0·94	8·85	10·3	14·3
8·08	1·6	8·08	0·65	0·65	5·72	7·0	18·0
(b) From Table 4							
0·90	10·0	0·90	0·01	0·45	6·60	7·1	4·9
1·00	10·0	1·00	0·01	0·50	7·27	7·8	6·1
2·00	10·0	2·00	0·04	1·00	13·33	14·4	9·1
3·10	10·0	3·10	0·10	1·55	19·00	20·7	15·4
4·00	10·0	4·00	0·16	2·00	22·86	25·0	21
6·00	10·0	6·00	0·36	3·00	30·00	33·4	36
8·00	10·0	8·00	0·64	4·00	35·55	40·2	47
10·00	10·0	10·00	1·00	5·00	40·00	46·0	50
(c) From Table 5(a)							
1·91	8·1	9·70	0·18	0·77	6·28	7·2	1·6
3·82	6·2	19·3	0·74	1·18	6·47	8·4	6·0
4·80	5·2	24·3	1·17	1·25	5·82	8·2	7·6
6·10	3·9	30·9	1·88	1·18	4·64	7·7	7·7
7·65	2·35	38·8	2·97	0·90	2·95	6·8	7·2
(d) From Table 6							
1·00	9·0	90	0·90	0·45	0·72	2·1	2·6
2·00	8·0	91	1·82	0·80	1·27	3·1	3·6
4·00	6·0	93	3·72	1·20	1·86	6·8	6·1
6·00	4·0	95	5·70	1·20	1·82	8·7	8·1
8·00	2·0	97	7·76	0·80	1·19	9·8	9·3

amount equivalent to the initial concentration of copper(II) bromide.

Considering the wide variation of conditions and of observed initial rate, the agreement between calculated and observed initial rates is remarkably good. Rate maxima are predicted as the catalyst concentration changes in those groups of experiments where maxima are observed, and the dominant kinetic order in diazoalkane in reactions in which lithium bromide had been added are pleasingly reproduced. There are only two serious discrepancies for which we can offer no explanation at this time. One is in experiments with high catalyst and low diazoalkane concentrations [Table 7(a)] where a fall in initial rate is predicted at high catalyst concentrations and an increase is observed. This may be evidence for an additional reaction mechanism perhaps involving interaction of two carbene copper complexes as has been from time to time sug-

If we assume for simplicity that k_3 is zero so that only azine is formed from the complex, then the rates of transformation of diphenyldiazomethane into azine (A) and ketone (K) are given by equations (5) and (6)

$$2\frac{d[A]}{dt} =$$

$$[Cu^{II}Br_2]_i[Ph_2CN_2]\left\{0{\cdot}05 + \frac{0{\cdot}8}{100[Br^-]+1}\right\} \quad (5)$$

$$d[K]/dt = 0{\cdot}01[Cu^{II}Br_2]_i[Br^-] \quad (6)$$

respectively. Division gives $d[A]/d[K]$ and, using the expression $[Ph_2CN_2]_0 - [Ph_2CN_2] = 2A + K$, equation 7 results. The multiplier b is a function only of the bromide ion concentration [equation (8)] and this is

$$-d[Ph_2CN_2]/d[K] = b[Ph_2CN_2] + 1 \quad (7)$$

$$b = (5[Br^-] + 0{\cdot}85)/([Br^-]^2 + 0{\cdot}01[Br^-]) \quad (8)$$

assumed constant over the whole of stage (ii) of the reaction at the levels given in Table 6. Integration of equation (7) between the limits $[Ph_2CN_2] = [Ph_2CN_2]_0$ and 0 then gives (9) relating the final ketone yield

$$[K] = b^{-1} \ln (b[Ph_2CN_2]_0 + 1) \qquad (9)$$

during stage (ii). To this must be added an additional amount of ketone, equal in concentration to the catalyst, liberated during stage (iii). The percentage of ketone produced is then given by equation (10) where

$$\frac{\% \text{ Ketone}}{100} =$$

$$\frac{[Cu^{II}Br_2]_i + b^{-1} \ln (b[Ph_2CN_2]_0 + 1)}{[Ph_2CN_2]_i} \qquad (10)$$

$[Ph_2CN_2]_i$ is the concentration of diazoalkane initially put into the reaction mixture. The calculated yields in Table 6 were obtained using equation (10) without correction for the formation of tetraphenylethylene. Since the olefin could arise as a by-product in either of the stages leading to azine, the observed yields of the two products should be combined in comparing them with calculation.*

Again the calculated values agree fairly well with the experimental findings. The overall fit might be improved somewhat by assuming that k_3 is not zero. It should be borne in mind, however, that the calculations are based on equations developed for initial rates of reaction. Since these equations may not hold throughout the course of the consumption of the diazoalkane, in particular because of the heterogeneous nature of the reaction mixture in the later stages, the agreement would seem to be acceptable. As expected, agreement between calculated and observed product proportions is worst where agreement between calculated observed initial rates is worst.

The reaction scheme which we have suggested can thus be made to fit the observed facts in at least a semi-quantitative way. We believe that it can form the basis of more detailed study. In particular, the present proposals throw little light on the detailed mechanism of the individual steps; these will require further experimentation. The present proposals cannot be simply extended to catalysis of the decomposition of diazoalkanes by copper(i) halides nor to catalysis by, for example, copper(ii) acetylacetonate. Preliminary investigations of such catalysis indicate quite different behaviour which may, we believe, be due in part to the greater difficulty in these cases in bringing about displacement of the ligands.[13]

EXPERIMENTAL

Materials.—Diphenyldiazomethane and acetonitrile were prepared and purified as previously described. Copper(ii) bromide was an anhydrous commercial sample used without further purification.

* An alternative source of tetraphenylethylene might be attack of $Ph_2CN_2^{+}$ on Ph_2CN_2.[11]

Kinetic Procedures.—Nitrogen evolution. The apparatus consisted of a two-limbed vessel into which the solutions of the diazoalkane and catalyst could be separately pipetted. The larger limb which was capable of holding all the reaction mixture had a flat bottom and contained a small magnetic stirrer. The volume of evolved nitrogen was measured in a horizontal 2 ml graduated pipette attached to the reaction vessel and closed by a short mercury drop, the position of which could be accurately read. Reactions were carried out at room temperature which varied by $<0.1°$ during the course of the reaction. After thermal equilibration of the apparatus and solutions, the reactants were mixed and the position of the mercury drop measured as a function of time. A typical experiment is shown in the Figure.

Visible spectrophotometry. The experimental technique has been described previously.[14]

I.r. spectrophotometry. The method previously described [1] was used, but, because the time of measurement was short compared with reaction times, it was unnecessary to quench the reaction mixture. Since Beer's law holds for the optical density of solutions of diphenyldiazomethane at 2040 cm^{-1} over the range of concentrations used in the kinetic experiments, initial rates for stage (ii) were determined graphically from plots of optical density against time. Downward curvature was found in first-order kinetic plots in the later stages of reaction, particularly at high catalyst concentrations.

Experiments under nitrogen were conducted in a two-limbed cell similar to one previously described for visible spectrophotometry [15] but carrying a sodium chloride cell. The cell was filled from time to time by inverting the cell and the spectrum recorded.

Stopped-flow Experiments.—The apparatus was of conventional design constructed and located at the Corporate Laboratory of I.C.I. Ltd. The change in optical density at 640 nm of solutions containing the catalyst and diazoalkane was displayed on a cathode ray oscilloscope and this trace was recorded photographically. Kinetic analysis of the traces was carried out using larger scale transcript of the photographic records.

Product Analysis.—The products, benzophenone, benzophenone azine, and tetraphenylethylene could all be isolated and were identified by comparison with authentic specimens.

Analyses were carried out by g.l.c. using a Pye 104 dual column gas chromatograph with flame ionisation detector fitted with 7 ft × 0.25 in glass columns containing 1% OV17 on Gas Chrom Q. Runs began at 150° until the ketone had been eluted, whereafter the temperature was raised by 6° min^{-1} to 270° to elute the olefin and azine. Response factors were determined relative to triphenylmethane as standard. Peak areas on chromatograms were determined using a Vidar 6300 digital integrator.

[13] D. S. Wulfman, B. W. Peace, and E. K. Steffen, *Chem. Comm.*, 1971, 1360.
[14] D. Bethell and R. D. Howard, *J. Chem. Soc.* (B), 1969, 745.
[15] D. Bethell, *J. Chem. Soc.*, 1963, 666.