Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 16.[1] Catalysis of the Decomposition of Diazodiphenylmethane by Copper(I) Bromide, Iodide, and Perchlorate in Acetonitrile

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The kinetics and products of decomposition of diazodiphenylmethane catalysed by copper(I) bromide, iodide, and perchlorate in acetonitrile solution have been investigated. All three salts convert the diazo-compound almost wholly into benzophenone azine, but small quantities of benzophenone are also produced. Copper(I) bromide and perchlorate both give rise to reactions showing the simple kinetic form $v = k[\mathrm{Cu^I}][\mathrm{Ph_3CN_2}]$, but the rate of decomposition of diazodiphenylmethane in the presence of copper(I) iodide is apparently independent of the concentration of the diazo-compound, although substituents therein alter the rate coefficient. Small amounts of paramagnetic precipitates form in reactions catalysed by the copper(I) halides, and reaction solutions are coloured when decomposition of the diazoalkane is complete. For a given catalyst concentration the order of catalytic efficiencies is CuI > CuBr > $\mathrm{CuClO_4}$.

It is shown that the rate coefficients observed in reactions catalysed by copper(I) bromide can be predicted with reasonable accuracy by an equation previously developed for copper(II) bromide catalysis. The relevance of this and the other findings to previous mechanistic studies is discussed.

IN the course of studies of the decomposition of diazodiphenylmethane brought about by copper(II) salts in homogeneous solution in acetonitrile we have identified two distinct mechanisms. The first is found using copper(II) perchlorate,[1,2] the metal ion oxidising the diazoalkane and the diazoalkane radical cation so produced taking part in a chain reaction in which the main product is tetraphenylethylene. The kinetic form of this reaction in anhydrous acetonitrile is very simple, and after initiation the copper appears to play no further part since almost identical rates and products are observed using a quite different one-electron transfer reagent tris(*p*-bromophenyl)ammoniumyl perchlorate. On the other hand, using copper(II) bromide as the catalyst, benzophenone azine is the predominant product, only traces of tetraphenylethylene are found, and the kinetic form of the reaction becomes more complicated.[3] The overall reaction takes place in a number of clearly identifiable stages with intermediate formation of copper complexes, and the rate law for the slowest stage shows a dependence on the concentration of bromide ions in the reaction medium. A central problem in this study and in related investigations by other groups [4-6] is the oxidation state of copper in the intermediate complexes (' copper carbenoids ').[7] In an effort to throw light on this matter, we have examined the catalysis of the decomposition of diazodiphenylmethane by three copper(I) salts in acetonitrile solution, the bromide, iodide, and perchlorate so that the kinetics and products of reaction could be compared directly with those from reactions catalysed by copper(II) salts.

RESULTS

Catalysis by Copper(I) *Bromide.*—Mixing of acetonitrile solutions of diazodiphenylmethane and copper(I) bromide leads to no instantaneous colour change as is found with reactions involving copper(II) bromide. During the course of the reaction, however, a dark green precipitate is formed which, when all the diazoalkane has been consumed, slowly redissolves with generation of the green colour which characterises solutions of copper(II) bromide in acetonitrile. The formation and later dissolution of the precipitate and the accompanying colour changes are identical with those observed in reactions catalysed by copper(II) bromide. In a typical experiment, a reaction mixture containing copper(I) bromide (4×10^{-3}M) was oxidised to the extent of *ca.* 70%. It should be noted that solutions of copper(I) bromide in acetonitrile appear to be perfectly stable indicating that the oxidation which is observed in these reaction mixtures is a consequence of the diazoalkane decomposition.

Because of the precipitate formation, kinetic experiments made use of the i.r. method used previously for copper(II) bromide catalysis. The copper(I) bromide-catalysed reactions show good first-order behaviour with respect to the diazoalkane; rate coefficients, k_{obs}, evaluated graphically are in Table 1. Extrapolation of first-order kinetic plots to zero time gives intercepts which show no evidence of rapid initial consumption of the diazo-compound. On increasing the concentration of the catalyst, a proportionate increase in k_{obs} is found, the average value of k_{obs}/[CuBr] being 0.94 ± 0.16 l mol^{-1} s^{-1}. A series of kinetic experiments was conducted with an excess of lithium bromide present (LiBr : CuBr = 4.9). The added salt gives, on average, a roughly four-fold reduction in k_{obs}/[CuBr] to 0.26 ± 0.01 l mol^{-1} s^{-1} (Table 2). At the highest concen-

TABLE 1

Observed first-order velocity constants for the reaction of diazodiphenylmethane (0.01M) with copper(I) bromide in acetonitrile at 30 °C

10^3[CuBr]/ M	10^3k_{obs} [a]/ s^{-1}	10^3k_{calc} [b]/ s^{-1}	Intercept/ %	Azine/ %
0.50	0.56	0.43	94	
1.00	1.2	0.85	98	96
2.01	2.1	1.7	98	94
3.01	2.8	2.6	94	91
4.02	3.1	3.4	90	80
5.02	3.8	4.3	92	70
6.50	4.8	5.5	90	*ca.* 75
8.05	7.8	6.8	98	75
8.78	8.1	7.5	98	
9.94	9.9	8.4	92	76

[a] Average value of k_{obs}/[CuBr] = 0.94 ± 0.16 l mol^{-1} s^{-1}.
[b] See Discussion.

tration of lithium bromide, however, the rate of disappearance of the diazodiphenylmethane is somewhat faster than expected on the basis of strict first-order kinetics.

Gas chromatographic examination of the reaction products showed that the diazo-compound is largely converted into two products, benzophenone azine and benzophenone. A trace of tetraphenylethylene could also be detected but this never amounts to more than 1% conversion of the diazoalkane initially present. The yield of azine decreases with increase in the copper(I) bromide concentration and on addition of lithium bromide as indicated in Tables 1 and 2.

TABLE 2

Effect of excess of lithium bromide on observed first-order velocity constants for reaction of diazodiphenylmethane (0.01M) with copper(I) bromide in acetonitrile at 30 °C

10^3[CuBr]/ M	10^3[LiBr]/ M	$10^3 k_{obs}$ [a]/ s^{-1}	$10^3 k_{calc}$ [b]/ s^{-1}	Intercept (%)	Azine (%)
1.99	9.8	0.55	0.9	96	76
3.99	19.6	1.05	1.3	88	44
5.98	29.4	1.5	1.7	97	43
7.98	39.2	2.0	2.0	97	20

[a] Average value of k_{obs}/[CuBr] = 0.26 ± 0.01 l mol^{-1} s^{-1}. [b] See Discussion.

Catalysis by Copper(I) *Iodide*.—Although there is no initial development of colour on mixing solutions of diazodiphenylmethane and copper(I) iodide in acetonitrile, reaction mixtures quickly take on an orange hue and a small amount of a dark brown gelatinous solid is precipitated. This material is paramagnetic (susceptibility 3.75×10^{-6} c.g.s. units). It does not redissolve at the end of the reaction as is found for the precipitates in the copper bromide reactions. The reaction products are formed in proportions which are independent of the catalyst concentration: benzophenone azine 94%, benzophenone 5%, tetraphenylethylene 1% for reaction mixtures initially 0.01M in diazodiphenylmethane.

The i.r. technique was again used for the kinetic studies and over about 75% of the reaction an essentially zero-order dependence on diazoalkane concentration is found. However, in the later stages of the reaction, especially if the initial concentration of diazodiphenylmethane was greater than 0.01M, the rate accelerates over that expected on the basis of a zeroth-order law. This effect is not very reproducible, although the initial rates are. Clearly the reaction is subject to some sort of autocatalysis rather than being truly zeroth order in the diazoalkane, and this is confirmed by our finding that 4,4′-dichlorodiazodiphenylmethane decomposes at about half the rate found for the unsubstituted diazo-compound under the same conditions. Initial rates, v_0, which probably refer to the true catalysis by copper(I) iodide are shown in Table 3. They show proportionality to the catalyst concentration. Addition of water had a negligible kinetic effect although it increased the yield of benzophenone at the expense of the azine.

Catalysis by Copper(I) *Perchlorate*.—This reaction proved to be the cleanest studied. No visible colour changes occur during the course of the reaction except that resulting from consumption of the diazo-compound; visible spectrophotometry (526 nm) can, therefore, be used to follow the progress of the reaction. A simple first-order dependence of the reaction rate on the diazoalkane concentration is observed; rate coefficients, k_{obs}, are given in Table 4 and are proportional to the concentration of copper(I) perchlorate, giving an average value of k_{obs}/[$CuClO_4$] of 0.385 ± 0.014 l mol^{-1} s^{-1}. Again the principal product is benzophenone azine, accompanied by some benzophenone, diphenylmethanol, and bisdiphenylmethyl ether. Addition of water had a small accelerating effect on the reaction rate and the yield of azine was slightly reduced.

TABLE 3

Observed zeroth-order velocity constants for the reaction of diazodiphenylmethane (0.01M) with copper(I) iodide in acetonitrile at 30 °C

10^4[CuI]/M	10^4 v_0 (mol l^{-1} s^{-1})
2.4	2.5 (2.6) [a]
4.8	5.3
9.6	10.2 (5.5) [b]
19.2	14.6
28.8	27.5
48.0	42.7

[a] H_2O (1M) present. [b] 4,4′-Dichlorodiazodiphenylmethane.

TABLE 4

Observed first-order velocity constants for the decomposition of diazodiphenylmethane (0.016M) by copper(I) perchlorate in acetonitrile at 30 °C

10^3[$CuClO_4$]/M	[H_2O]/M	$10^3 k_{obs}$ [a]/s^{-1}	Azine (%)
1.0		0.40	
3.1		1.2	
5.4		1.7	76
	0.20	2.0	70
	0.70	2.5	59
	1.36	2.5	60
7.2		2.6	
10.4		4.0	
14.4		5.6	
17.9		6.5	
23.3		9.0	

[a] Average value of k_{obs}/[$CuClO_4$] = 0.385 ± 0.016 l mol^{-1} s^{-1}.

DISCUSSION

Copper(I) *Bromide Catalysis*.—This reaction shows apparently simple kinetic behaviour, a first-order dependence of the reaction rate on both diazodiphenylmethane and the catalyst, in contrast to the complexities of the reaction induced by copper(II) bromide. It is to be noted, however, that when the effects on the composition of copper(II) bromide reaction mixtures resulting from the initial very rapid processes have been largely eliminated by using a constant excess of diazoalkane over the catalyst, the kinetic form is simplified, and the apparent second-order rate coefficient (k_{obs}/[$CuBr_2$]) is then very similar to that observed in reactions catalysed by copper(I) bromide. Moreover, the reactions catalysed by the two copper bromides show marked similarities in their later stages (precipitate formation and generation of the green colour after the disappearance of the diazoalkane). In Tables 1 and 2 we have, therefore, included rate constants, $k_{calc} = -\{d[Ph_2CN_2]/dt\}_{t=0}/[Ph_2CN_2]_0$, calculated using the equation

$$-\left\{\frac{d[Ph_2CN_2]}{dt}\right\}_{t=0} =$$

$$[\text{Catalyst}]\left\{0.01[Br^-] + 0.05[Ph_2CN_2] + \frac{0.8[Ph_2CN_2]}{100[Br^-] + 1}\right\}$$

previously developed to pattern the kinetic behaviour of reaction mixtures containing diazodiphenylmethane, copper(II) bromide, and lithium bromide in acetonitrile. The agreement is remarkably good and this encourages us to believe that, after the initial mixing of reagents, the catalytic system is the same whether the copper bromide added is the copper(II) or copper(I) salt. This inference still leaves open the question of whether the copper complexes involved contain copper at the +1 or +2 oxidation level (but see below).

Copper(I) *Iodide Catalysis*.—Copper(I) iodide is the most effective of the three catalysts in bringing about decomposition of diazodiphenylmethane. On the basis of initial rates, the second-order rate coefficient ($v_0/[\mathrm{CuI}][\mathrm{Ph_2CN_2}]$) is 98 ± 13 l mol^{-1} s^{-1}, two orders of magnitude greater than for the bromide. However, the colour changes which occur as the reaction progresses indicate a more complicated state of affairs. One possible complication is the generation of iodine which is an extremely potent catalyst for the decomposition of diazoalkanes.[8] In particular, iodine catalysis of the decomposition of diazodiphenylmethane leads almost exclusively to the formation of benzophenone azine at a rate which is proportional to the diazoalkane concentration but approaches a second-order dependence on iodine.[8b]

Copper(I) *Perchlorate Catalysis*.—The reaction shows clean second-order kinetics under the conditions studied with a second-order rate coefficient rather less than half that observed for copper(I) bromide under comparable conditions. In this instance the copper species in solution is presumably the copper(I) cation tetrahedrally solvated by acetonitrile molecules. These ligands should be easily displaceable by the diazoalkane, the rate-limiting step then being loss of nitrogen to generate the copper carbenoid. The absence of nucleophilic anions would be expected to simplify the available pathways to products compared with catalysis by copper bromide, but we cannot rule out the possibility that further copper(I) complexes could be involved in the perchlorate case. It is clear, however, both on the basis of reaction products and the 300-fold difference in second-order velocity constants, that catalysis by copper(I) perchlorate involves quite a different mechanism from that induced by copper(II) perchlorate. The copper(II) salt initiates a radical-cation chain process leading largely to tetraphenylethylene as shown in the preceding paper,[1] whereas copper(I) perchlorate yields predominantly benzophenone azine by way of intermediate copper complexes.

The remaining question is therefore why different reaction pathways are not observed for copper(I) and copper(II) bromides. The fact that copper(I) perchlorate brings about the decomposition of diazodiphenylmethane with a second-order rate coefficient of 0.385 l mol^{-1} s^{-1} while copper(I) bromide yields a value of 0.94 l mol^{-1} s^{-1} suggests that in both cases the major reaction pathway may involve an intermediate complex containing copper in the +1 oxidation state. This conclusion is the reverse of that previously reached rather tentatively on the basis of our study of copper(II) bromide catalysis, and is in line with Kochi's views based on work with the copper trifluoromethanesulphonates. If the active complexes are indeed copper(I) complexes, then an explanation is required for the failure of copper(II) bromide to initiate the radical-ion chain reaction since the diazoalkane is likely to be the reducing agent. The bromide ions present in solution could be responsible for inhibiting this pathway by rapidly capturing any radical ions produced; the resultant electrically neutral radicals could, if not further oxidised, dimerise yielding 1,2-dibromotetraphenylethane. Although this product was not detected, the corresponding diacetate has been obtained in good yield on treatment of diazodiphenylmethane with copper(II) acetate in dimethylformamide.[9]

EXPERIMENTAL

The products and kinetics of reactions were determined by the methods previously used in investigating catalysis by copper(II) salts.[1,3]

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