The Initiation of Acid-Catalyzed Decomposition of Diazodiphenylmethane by Cation Radical Reactions

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Bakke, J. M., Bethell, D. and Parker, V. D., 1987. The Initiation of Acid-Catalyzed Decomposition of Diazodiphenylmethane by Cation Radical Reactions. – Acta Chem. Scand., Ser. B 41: 253–256

In dry acetonitrile or in solvents containing water or methanol, diazodiphenylmethane undergoes catalytic decomposition upon the anodic generation of a low concentration of the corresponding cation radical. This catalytic decomposition is effectively inhibited by low concentrations of 2,6-lutidine. These observations suggest the proton to be the chain carrier and a comparison of the observed kinetic behaviour with that previously reported for the perchloric acid catalyzed decomposition confirms this interpretation.

The anodic decomposition of diazodiphenylmethane (Ph_2CN_2) in acetonitrile solution was studied in detail some fifteen years ago[1] and it was concluded that a chain reaction was initiated and sustained by the cation radical generated upon oxidation of the diazo-compound giving rise to the final product, viz. tetraphenylethylene. A subsequent kinetic study of the decomposition of Ph_2CN_2 brought about by copper(II) perchlorate or tris(4-bromophenyl)ammoniumyl perchlorate in dry acetonitrile was interpreted[2] in terms of the same mechanism. On addition of water, however, the mechanism changed, showing all the characteristics[3] of a proton acid catalysed reaction in which the key intermediate is the diphenylmethyl cation, which could be partitioned between attack on water (giving diphenylmethan-

ol) or on substrate (giving tetraphenylethylene), with regeneration in each case of a proton (Scheme 1). The similarity of the products of acid-catalysed and anodic decomposition of Ph_2CN_2 in acetonitrile (though not in less polar solvents) suggested to us the possibility that at least part of the reaction believed to be catalysed by the cation radical might, in fact, result from acid catalysis. There have been a number of recent reports of reactions catalysed by ammoniumyl salts, apparently via cation radicals, which have subsequently been shown to have involved proton transfer mechanisms.[4]

This possibility has now assumed added importance. The recent observations that certain diazocompounds form, on electroreduction, anion radicals which undergo unimolecular loss of ni-
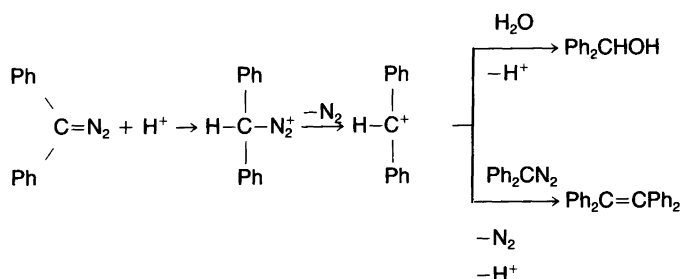
Scheme 1.

trogen to give carbene anion radicals in solution[5] prompted us to reinvestigate the electrooxidation of Ph_2CN_2 in acetonitrile solution, in search of evidence of the formation of the corresponding carbene cation radical $Ph_2C^{+\cdot}$. It was felt that the ambiguity attached to the earlier work left the possibility that the carbene cation radical, which had been excluded as an intermediate, might be generated following a change in the reaction conditions. Our first step in this direction was to reinvestigate the anodically initiated chain reaction, and the results are presented here.

Methods and results

Kinetic method. The solution of substrate in acetonitrile/$Bu_4N^+BF_4^-$ (0.1 M) was placed in one compartment of a two-compartment cell thermostatted to 290 K. Both compartments of the cell were equipped with gas inlet tubes and platinum gauze electrodes. The compartment containing substrate was provided with a small indicator electrode (diameter = 0.4 mm) and an Ag/Ag^+ reference electrode. Stirring was controlled by adjusting the flow of gas, i.e. nitrogen or oxygen, into the solution through the gas inlet tubes. Derivative cyclic voltammograms (DCV) for the oxidation of substrate were processed at 10.0 s intervals by the data retrieval system described in a previous paper.[6] Five voltammograms were processed, to relate the derivative peak heights to the initial substrate concentration, before the chain reaction was initiated. The chain reactions were initiated by constant current oxidation of the substrate to the desired degree of conversion while continuing the periodic DCV analysis. The decay of the substrate as a function of time was followed by the decrease in peak height for the substrate oxidation. The analysis was continued until the substrate could no longer be detected.

Kinetic results. Table 1 gives the results of two experiments in which Ph_2CN_2 (5 mM) was decomposed in CH_3CN/Bu_4NBF_4 (0.1 M) containing water or deuterium oxide (69.5 mM) by anodic oxidation (a current of ca 10 mA for 15 s) in air. The results are expressed in terms of the time, in units of the half-life ($t_{1/2}$), required for the normalized concentration to fall to a specified level. It can be seen that the results are in fair agreement with the theoretical behaviour for first-or-

Table 1. Deuterium kinetic isotope effect during the chain decomposition of $Ph_2C=N_2$ in acetonitrile containing water (69.5 mM).[a]

C_N[b]	$t/t_{1/2}$(theor.)[c]	$t/t_{1/2}(D_2O)$[d]	$t/t_{1/2}(H_2O)$[e]
1.00	0	0	0
0.95	0.074	0.110	
0.90	0.152	0.210	
0.85	0.235	0.303	0.349
0.80	0.322	0.390	0.421
0.75	0.415	0.474	0.521
0.70	0.515	0.563	0.628
0.65	0.622	0.644	0.698
0.60	0.737	0.769	0.777
0.55	0.863	0.878	0.878
0.50	1.000	1.000	1.000
0.45	1.152	1.159	1.156
0.40	1.322	1.325	1.360
0.35	1.515	1.515	1.595
0.30	1.737	1.747	1.823
0.25	2.000	2.04	2.11
0.20	2.322	2.39	2.48
0.15	2.737	2.87	2.98
0.10	3.322	3.58	3.73
0.05	4.322	4.90	5.13

[a]In solvent containing Bu_4NBF_4 (0.1 M) at 290 K. [b]Normalized concentrations. [c]First-order rate law. [d]$t_{1/2}$ = 107 s. [e]$t_{1/2}$ = 32.8 s.

der disappearance of Ph_2CN_2 over 80 % reaction and that the reaction shows a kinetic hydrogen isotope effect of 3.3 at the reaction temperature of 290.0 K. The latter result, which corresponds exactly with the isotope effect measured for perchloric acid catalyzed decomposition of Ph_2CN_2 in acetonitrile,[3] indicates that the chain reaction initiated at the anode is one in which proton transfer is the rate-limiting step.

The effect of variation in the concentration of water added to the solvent/electrolyte system is shown by the results in Table 2. The reactions were carried out in nitrogen-purged solutions and the results show that as the water concentration is lowered progressively, the first-order rate coefficient, k_{app}, measured after passage of a fixed initiating current (22.5 mA for 15 s) rises monotonically, the highest rate being measured for a solution to which activated alumina had been added so as to eliminate as far as possible traces of water. Again, these results parallel the behaviour observed for perchloric acid catalyzed reactions

Table 2. The effect of water on the rate of decomposition of Ph_2CN_2 in acetonitrile.[a]

$[H_2O]/mM$	$t_{1/2}/s$	$10^2 k_{app}/s^{-1}$
over Al_2O_3	12.4	5.59
69.5	21.2	3.27
139	34.7	2.00
278	89.1	0.78
556	235	0.30

[a]Reaction in solvent containing Bu_4NBF_4 (0.1 M) at 290 K. Initiated by 15 s electrolysis at 22.5 mA, equivalent to an initiator concentration of 0.175 mM. Substrate concentration equal to 5.0 mM.

or $Cu(ClO_4)_2$ catalyzed reactions with added water.

Addition of methanol has a similar effect. The results in Table 3 show, in addition, that the rate of the chain reaction is reduced substantially in the presence of oxygen, particularly in the absence of added methanol. It should also be noted that varying the initial period of electrolysis, which changes the nominal initiator concentration over a two-fold range, leads to an approximately linear change in rate:

$$k_{app} = 109.2 \text{ [initiator]} - 0.0077.$$

This expression is of very similar form to that ob-

Table 3. The effect of methanol on the rate of decomposition of Ph_2CN_2 in acetonitrile.[a]

$[CH_3OH]/mM$	Atmosphere	$t_{1/2}/s$	10^2 k_{app}/s^{-1}
0	O_2	20.9	3.32
	N_2	11.8	5.87
77	O_2	21.6	3.21
154	O_2	28.3	2.45
310	O_2	32.9	2.11
620	O_2	65.5	1.06
		$(126)^b$	$(0.55)^b$
		$(38.1)^c$	$(1.82)^c$
	N_2	52.3	1.33

[a]Reaction in solvent containing Bu_4NBF_4 (0.1 M) at 290 K in an oxygen atmosphere. Initiated by 15 s electrolysis at 22.5 mA, equivalent to an initiator concentration of 0.175 mM. Substrate concentration equal to 5.0 mM. [b]Initiated by 10 s electrolysis at 22.5 mA. [c]Initiated by 20 s electrolysis at 22.5 mA.

served for reactions initiated by $Cu(ClO_4)_2$ or $Ar_3N^{+\cdot}ClO_4^-$ in nominally anhydrous CH_3CN at 303.2 K.

Finally, it was observed that under the conditions employed the chain reaction could be inhibited by addition of 2,6-lutidine at a concentration equivalent to that of Ph_2CN_2. Under these conditions the diazo compound could be decomposed anodically in a non-chain process, interruption of the current leading to no further disappearance of Ph_2CN_2. The anodic decomposition of diazo compounds in the presence of 2,6-lutidine will be the subject of a future report.

Reaction products. The products were identified by GC/MS analysis (Hewlett-Packard 5985, SE30-fused silica coloumn). Quantitative analyses were performed by the internal standard method on a Carlo-Erba 4160 GC (25 m SE30-fused silica; *p*-nitrotoluene internal standard for benzhydrol methyl ether, anthracene for tetraphenylethylene and dibenzhydrol ether). Authentic samples of the identified products were prepared by known methods.

An exhaustive study was not undertaken. It was established, however, that under nominally anhydrous conditions, the products of chain decomposition of Ph_2CN_2 (10 mM) included tetraphenylethylene (corresponding to 45 % of the diazo-compound initially present) and bis(diphenylmethyl) ether (20 %). Diphenylmethanol and benzophenone azine were not determined in this analysis. In the presence of added methanol at concentrations in the range 100 to 800 mM, Ph_2CN_2 (5 mM) yielded exclusively diphenylmethyl methyl ether when reactions were conducted under an oxygen atmosphere. Under nitrogen, the yield of the methyl ether dropped to 71 % at the highest methanol concentration (800 mM) and this was further reduced to 51 % when the initial concentration of Ph_2CN_2 was 2.5 mM.

Discussion

The present investigation establishes that the chain reaction which is initiated by anodic oxidation of Ph_2CN_2 is one in which proton transfer to the diazo carbon is the rate-determining step. The evidence supporting this is as follows:

(i) The reaction is completely inhibited by 2,6-lutidine.

(ii) Reducing the concentration of added hydroxylic compounds, water or methanol, progressively to zero leads to a monotonic increase in reaction rate, as found for perchloric acid catalyzed reactions in CH_3CN solution.[3].

(iii) In the presence of water (69.5 mM), the reaction shows a kinetic hydrogen isotope effect of 3.3, very similar to that observed for the perchloric acid catalyzed reaction.[3]

(iv) The observed reaction products are consistent with partitioning of an intermediate carbenium ion (Ph_2CH^+) between attack on substrate or on hydroxyl groups (present as water, methanol or, in the later stages of reactions with low levels of water, diphenylmethanol). This has been observed for reactions of the carbene Ph_2C: generated by thermolysis of Ph_2CN_2 in dry CH_3CN.[7]

The source of the acid catalyst is presumably the combination of the diazoalkane cation radical (or one derived from it) and the protic nucleophiles present at a significant level even in the carefully dried solvent. Acetonitrile containing 10 mM water is 99.98 % pure. The effect of carrying out experiments under nitrogen might well be to protect the initially formed cation radical from reaction with oxygen, thereby permitting it to select the protic nucleophile and then to initiate acid catalysis.

The results of the present investigation conflict in one important respect with those reported earlier[2] for the reaction of Ph_2CN_2 (16.6 mM) with $Cu(ClO_4)_2$ or $Ar_3N^+\cdot ClO_4^-$ in acetonitrile. In the earlier work, it was found that at low concentrations (<ca. 300 mM) of added water the rate of disappearance of Ph_2CN_2 passed through a maximum. At higher water concentrations the rate was reduced, as found in the perchloric acid catalysed decomposition of Ph_2CN_2 and in the present investigation. However, the rate also decreased at lower water concentrations and in this region the observed kinetic hydrogen isotope effect also decreased to a limiting value of 1.0 in the nominally anhydrous solvent. It would seem that the acid-catalyzed reaction must have been suppressed under these conditions, and in the case of reactions with $Cu(ClO_4)_2$, this might have permitted a copper-catalyzed pathway to become detectable. A pathway of this kind, involving an organometallic intermediate, has been proposed to account for the predominance of *cis*-stilbene in the products of decomposition of phenyldiazomethane catalyzed by copper salts.[1] Such an interpretation is not feasible in the case of the reactions catalyzed by the ammoniumyl salt (where the rate decrease at low water concentrations was less pronounced); the discrepancy here remains a mystery that only further experimentation will resolve.

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