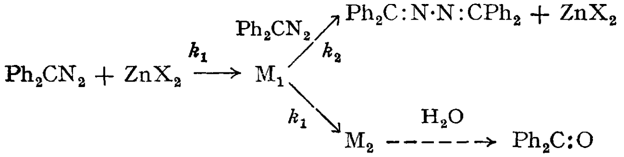
Kinetics and Mechanism of the Decomposition of Diazoalkanes catalysed by Zinc Halides

By D. BETHELL* and K. C. BROWN

(*The Robert Robinson Laboratories, The University, Liverpool,* 7)

ALTHOUGH the reaction of Lewis acids with diazoalkanes is of considerable importance for the preparation of organometallic compounds,[1] the reaction mechanism has not received the intensive study devoted to Brönsted acid-induced reactions of diazo-compounds.[2] The reaction of diazoalkanes with zinc halides, particularly the iodide, is of special importance because the initial product is thought[3] to be related to the reactive organometallic intermediate of the Simmons–Smith cyclopropane synthesis.[4] We report here a preliminary kinetic and product study of the reaction of the zinc halides with diphenyldiazomethane and diazofluorene in acetonitrile which throws some light on the mechanism.

Chart 1



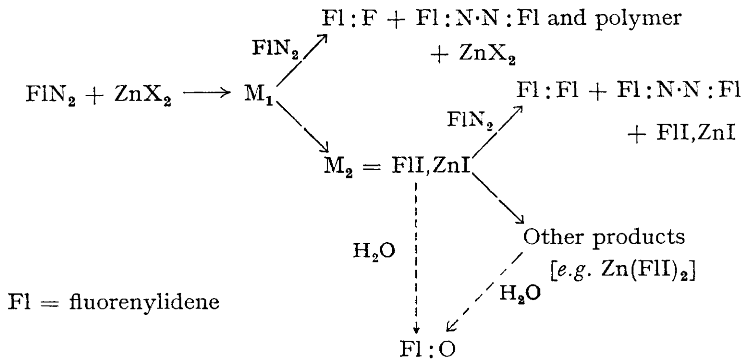
M_1 and M_2 are intermediates.

Diphenyldiazomethane (6·7—42·5 × 10^{-3}M) decomposes in the presence of zinc chloride or bromide (0·7—10·1 × 10^{-3}M) in acetonitrile to give, after an aqueous work up, benzophenone and its azine only.[5] The product proportions and the kinetics of disappearance of the diazo-compound fit the simple scheme shown in Chart 1, with k_1 = 16 l. mole^{-1} min.$^{-1}$ and k_2/k_3 = 500 l. mole^{-1} for $ZnCl_2$, and k_1 = 35 l. mole^{-1} min.$^{-1}$ and k_2/k_3 = 260 l. mole^{-1} for $ZnBr_2$, at 30°.

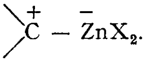
With zinc iodide (~10^{-5}M), the decomposition of diphenyldiazomethane (~10^{-2}M) shows quite different kinetic behaviour: some 80% of the diazoalkane decomposes in an initial rapid stage, complete in about 2 min. at 30°, and the remainder disappears much more slowly according to the rate law $v = k_S[Ph_2CN_2][ZnI_2]_0$, where $[ZnI_2]_0$ is the stoicheiometric zinc iodide concentration and k_S has the value ~3000 l. mole^{-1} min.$^{-1}$. Again the only products of the reaction are benzophenone and its azine, but, at a given initial concentration of diazoalkane, the yield of azine is much lower with zinc iodide than with the chloride and bromide.

A similar pattern of kinetic behaviour is observed in the decomposition of diazofluorene (FlN_2) induced by the zinc halides. From spectrophotometric observation of the reaction rate in very dilute solutions of diazofluorene, second-order velocity constants (in l. mole^{-1} min.$^{-1}$ at 30°) corresponding to k_1 in Chart 1 were found to be: $ZnCl_2$, ~2; $ZnBr_2$, ~4; ZnI_2, ~200. The slow stage of the zinc iodide induced decomposition had k_S = 8 l. mole^{-1} min.$^{-1}$. However, the reaction products do not show the simple pattern found with diphenyldiazomethane: not only do the identifiable products (bifluorenylidene, fluorenone, and its azine, and 9-halogenofluorenes) not account for all the initial diazoalkane, but, when the reaction is carried out in air rather than under nitrogen, the yield of bifluorenylidene, though not of azine, is markedly reduced. Clearly a more complex reaction scheme is involved.

Chart 2



Treatment of 9,9-di-iodofluorene with excess of zinc–copper couple[6] in acetonitrile in the dark and under a nitrogen atmosphere gives, after filtration, a solution which we assume, for present purposes, to contain 9-(9-iodofluorenyl) zinc iodide (FlI,ZnI). Treatment of the solution with water gives fluorenone in quantitative yield based on di-iodofluorene. Diazofluorene ($2{\cdot}48 \times 10^{-2}$M) decomposes when treated with FlI,ZnI ($3{\cdot}34 \times 10^{-3}$M) in acetonitrile under nitrogen to give bifluorenylidene (66% based on diazoalkane), fluorenone azine (11%), and fluorenone (corresponding to the residual diazo-compound + organometallic reagent): in air, the fluorenone yield is increased largely at the expense of bifluorenylidene.† The decomposition obeys the rate law $v = k[FlN_2][FlIZnI]$ with k = 8·4 l. mole^{-1} min.$^{-1}$ at 30°. The similarity of this value to that of k_S for the slow stage of the zinc iodide-catalysed decomposition of diazofluorene suggests that the same organometallic intermediate is involved in both reactions.

Accordingly, we formulate the decomposition of diazofluorene induced by zinc halides as in Chart 2. It is a plausible assumption that M_1 in Charts 1 and 2 is a zwitterionic species of the type  $>\overset{+}{C}-\overset{-}{ZnX_2}$. For X = Cl or Br, this intermediate reacts readily with further diazoalkane to give products, with regeneration of the zinc halide, much more rapidly than it rearranges to give the second intermediate M_2. For X = I, more of M_1 is diverted to M_2, with consumption of zinc iodide, so that a point is reached when M_2 is the only catalytically active species present. A slower decomposition of the diazoalkane then ensues.

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† 9,9-Di-iodofluorene also brings about the decomposition of diazofluorene but gives very little bifluorenylidene. The major product appears to be 9,9'-di-iodo-9,9'-bifluorenyl.

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