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THE EFFECT OF ION-PAIRING ON THE COURSE OF DECOMPOSITION OF A DIAZONIUM SALT (1)

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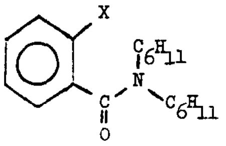
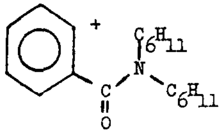
We wish to present results which suggest that ion association can strongly influence product composition in a diazonium salt decomposition.

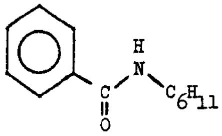
Thermal decomposition in various solvents of N,N-dicyclohexylbenzamide *o*-diazonium (I) bisulfate (prepared *in situ*) and fluoroborate (preformed) furnishes N-cyclohexylbenzamide (VII), products (II-IV) in which the diazonium function has been replaced by various nucleophiles, and small quantities of two unidentified products. The dealkylation product (VII) is produced along with cyclohexanone by a reaction in which the benzene carbonium ion (VI) suffers an intramolecular hydride ion transfer. (2)



I - X = N_2^+ III - X = F
II - X = OH   IV - X = OMe
V - X = Cl



VI



VII

The product yields in various solvents, after aqueous work-up, are shown in Table I. Noteworthy features include (a) a sharp decrease

TABLE I

Thermal Decomposition of N,N-Dicyclohexylbenzamide o-Diazonium Salts

Anion[a]	Conc. $M \times 10^{-2}$	T°C	Time min.	Solvent $(M_{H_2O})(M_{H_2SO_4})$	Products (% yield)[b,c,d]	Total Yield[e]
B	9.9	80	60	AcOH(2.1)(0.96)	II(40), VII(13)	88
B	10.4	90	90	AcOH(9.3)(0.83)	II(32), VII(32)	71
B	8.1	80	100	AcOH(21)(0.63)	II(16), VII(67)	92
F	12.9	70	60	AcOH	II(41), III(30), VII(13)	84
F	3.1	40	4,320	MeOH	IV(26), III(2), VII(41)[f]	82
F	9.5	60-67	34	MeOH(0)(0.71)	IV(11), II(5), VII(79)	101
F	13.3	26	180	MeOH(0)(1.0)	IV(5), II(2), VII(81)	93
F	9.5	26	180	MeOH(16)(1.0)	IV(0), II,[g] VII(86)[f]	g

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[a] B = Bisulfate, F = Fluoroborate. [b] Determined by isolation except where noted. [c] Small amounts (1-6%) of compounds of unknown structure are formed in most cases but are not recorded in the Table. [d] Products have been subjected to acidic hydrolysis at room temperature. [e] Includes unreacted starting material, where appropriate, and unknown compounds. [f] Yields by gas chromatography. [g] The presence or absence of phenol could not be determined by the gas chromatographic method used in this run.

in the yield ratio of phenol (II) to hydride transfer product (VII) as the water content of the acetic acid medium in which the bisulfate is decomposing increases (b) in the fluoroborate case, a striking decrease in yield of Schiemann product (III) in going from acetic acid to methanol (3), (c) the production of 41% aryl acetate (hydrolyzed during work-up to phenol II) when the fluoroborate is decomposed in acetic acid, but only 26% of methyl ether (IV) when the same salt is decomposed in the more nucleophilic solvent methanol (3) and (d) a steep decrease in the yield ratio of methyl ether (IV) to hydride transfer product (VII) as the decomposition medium is changed from methanol through methanol-sulfuric acid to methanol-sulfuric acid-water.

An unmistakable relationship exists between product composition and polarity of the solvent. These results can be reasonably interpreted if it is assumed that decomposition of "free," or unpaired diazonium ions, present in the more polar solvents, yields almost exclusively hydride transfer products, while ion pairs lead mainly either to reaction of the carbonium ion VI with the anion to produce aryl fluoride or aryl hydrogen sulfate (hydrolyzed in work-up to phenol) or with solvent to produce methyl ether, phenol or aryl acetate (hydrolyzed in work-up to phenol), as the case may be. This interpretation implies that the presumed carbonium ion intermediate (VI) preferentially undergoes an intramolecular hydride ion transfer rather than reaction with solvent *unless the anion is associated with the cation-solvent complex*. The presence of the anion apparently promotes the reaction of solvent with the cation.

When the same diazonium fluoroborate is thermally decomposed in a series of chlorinated hydrocarbon mixtures of known dielectric constants (conc. of salt = 3.07 ± .06 M; temp. = 40°), the main product is aryl fluoride (III), the yield of which increases smoothly from 47.1% to 85.5% as the dielectric constant decreases from 9.54 (ethylene chloride) to 3.02 (carbon tetrachloride-chloroform). Another important product is aryl chloride (V) which apparently arises by *abstraction of a chloride ion from the solvent by the benzene cation VI*. This appears to be the first case of such a chloride ion abstraction and its occurrence in chloroform is further confirmation that these reactions are not radical in nature (2,4a). The yield of aryl chloride decreases sharply from 34.2% to 4.9% as the dielectric constant decreases. The yields of hydride transfer product (VII) and the unknown compounds are fairly small and do not follow a consistent pattern.

Using an ion pair dissociation constant of 1.0×10^{-4} in the most polar of the solvents, ethylene chloride, (5) it can be calculated that only about 10% of the product in that solvent is derived from free ions. Therefore, both the fluoride and chloride are probably derived from associated ions. Since the yields of fluoride and chloride respond in an opposite manner to changes in dielectric constant of the medium, it is likely that they are derived from different species. We suggest that the fluoride (III) is derived from inner (intimate) (6) ion pairs (ion dipoles) (7) and/or higher aggregates, while the reaction product with solvent (V) is derived from outer [solvent separated (6) or Bjerrum (7)] ion pairs (8). It is not unreasonable to assume that the aryl acetate and ether of Table I are also derived from outer ion pairs.

The concept that molecules in the bulk solvent may be less capable of reacting with carbonium ions than those within ion pairs is not only intuitively satisfying but it may offer a partial explanation of the retention of configuration that is sometimes observed in certain solvolysis reactions (9,10). In general, it appears that studies of the behavior of these relatively stable ion pairs may be of great value in understanding the reactions of the more transient ion pair intermediates.

References and Footnotes

1. Supported by the National Science Foundation through Grant NSF G-23705.
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3. The temperature difference in these two runs is presumably not responsible for this change. The distribution of products in reactions of this type is notably insensitive to temperature (4).
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5. The constants for several salts in that solvent are close to this value. W. E. Thompson and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1016 (1947).
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8. An alternative explanation for the behavior of the yields of fluoride and chloride is that the ability of the solvent molecules to donate chloride ions approximately parallels the dielectric constants of the media. An attempt is now being made to distinguish between these explanations.
9. T. Cohen and E. Jankowski, *Abstracts of Papers*, 147th Meeting of The American Chemical Society, Philadelphia, Pa., April 1964, p. 47N.
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