STUDIES IN PHYSICAL ORGANIC CHEMISTRY

"KINETIC STUDIES OF THE THERMOLYSIS OF SOME CINNAMOYL AZIDES"

By

MADLENE LOTFY ASKANDAR

B. Sc. (Hons.)

A THESIS

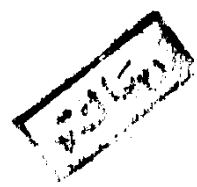
Submitted for the Degree

of Master of Science

Ain Shams University

Faculty of Science

Chemistry Department



CAIRO

1972

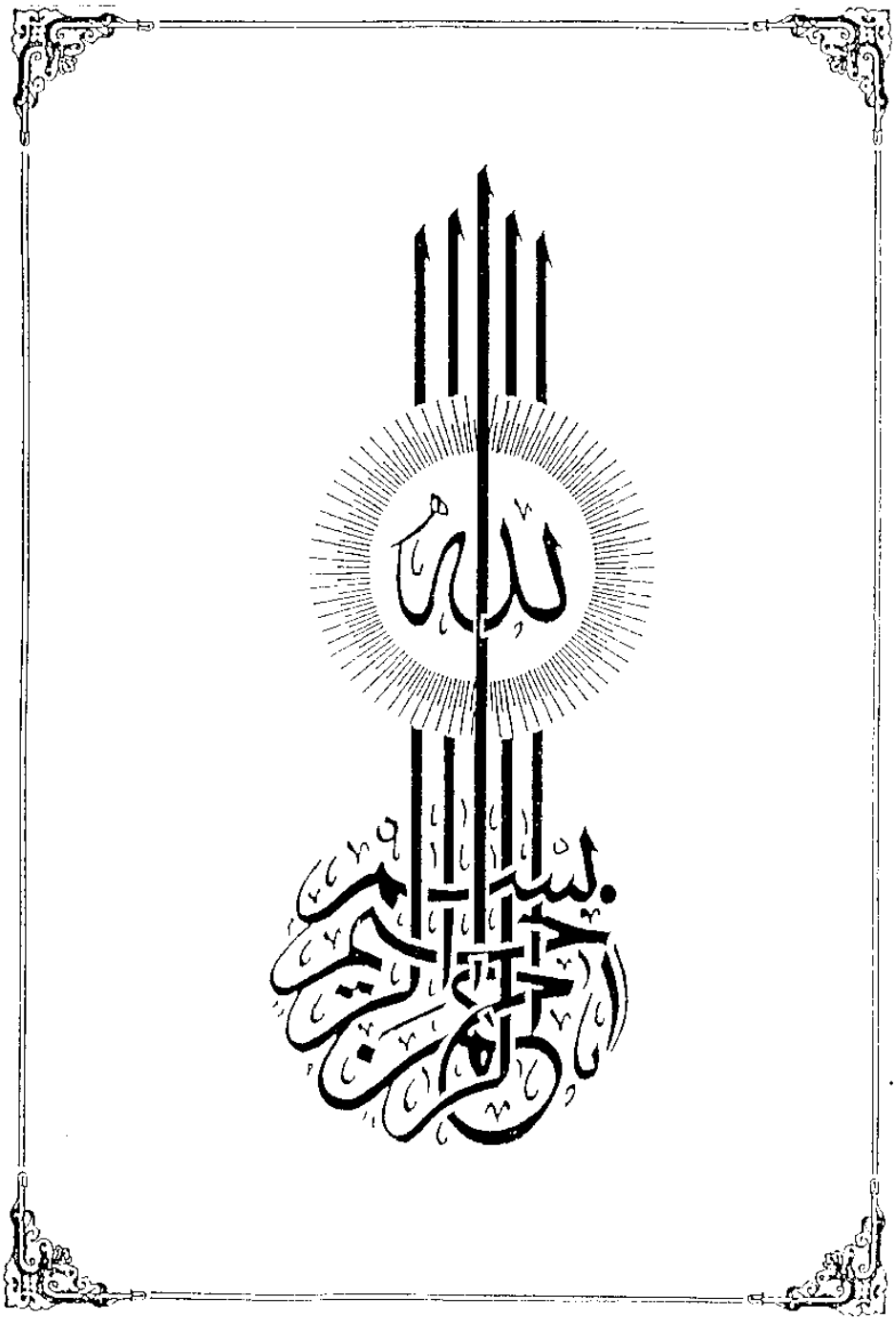
STUDIES IN PHYSICAL ORGANIC CHEMISTRY

"Kinetic Studies of The Thermolysis of Some Cinnamoyl Azides."

Thesis Advisers	Approved
Professor W.I. Awad (D.Sc.)	- - - - - - - - - - - -
Assist. Prof. S. Nashed	- - - - - - - - - - - -

Professor S.K. Tobia

Head of Chemistry Department



ACKNOWLEDGEMENT

All the work recorded in this thesis is original unless otherwise stated by references. This work was carried out in the Research Laboratories of Kinetics, Department of Chemistry, Faculty of Science, Ain Shams University.

The author wishes to express his deep thanks to Professor S.K. Tobia, Head of Chemistry Department, Faculty of Science, Ain Shams University, for the facilities at his disposal.

The author wishes to express her deep appreciation and gratitude to Professor W.I. Awad, D.Sc., Head of Chemistry Department, College for Women, Ain Shams University for suggesting problems, valuable guidance, help and advice throughout the progress of this work.

The author is also indebted to Dr. S. Nashed, Assistant Professor of Physical Chemistry and Dr. S.S.M. Hassan, Lecture of Chemistry for their continuous help and advice throughout the work.

M.L Askandar

Department of Chemistry
Faculty of Science
Ain Shams University
Egypt

N O T E

The candidate has attended postgraduate course for two years in the following topics :

1) Mechanisms of Organic Reactions
2) Organic Microanalysis.
3) Electronic, Infrared, Nuclear Magnetic Resonance, Raman, and Mass Spectroscopy of Organic Molecules.
4) Organic Reactions.
5) Chemistry of Heterocyclic Compounds.

She has successfully passed a written examination in these courses.

Prof. S.K. Tobia

Head of Chemistry Department

C O N T E N T S

S U M M A R Y

The thermolysis of cinnamoyl azide and p-methoxy, p-nitrocinnamoyl azides was studied kinetically at different temperatures and in different solvents (e.g. benzene, aniline, acetic acid).

The reaction is proved to be first order reaction for all azides investigated in all solvent used. The rate of the reaction was followed by two different methods. The first one is gasometric method in which the volume of nitrogen produced through the decomposition reaction is collected and measured. The second one is a titrimetric method in which the isocyanates produced are titrimetrically determined by reaction with n-butylamine followed by acidimetric finish. The values obtained by the two methods are in good agreement and provides mutual evidence to the satisfactory and successful performance of both the gasometric and titrimetric techniques.

The substituent groups have little effects on the rate of reaction. Since p-electron releasing groups decrease the rate of reaction and p-electron attracting groups increase the rate of reaction. This is due to the ease of breaking of $\overset{1}{N}\text{-}\overset{2}{N}$ bond. The second effect of substituent is stabilization or destabilization the molecule in transition state.

The solvent effect is found to be of the following order:

$$K_{acetic} > K_{aniline} > K_{benzene} \quad \text{and}$$

$$E_{acetic} < E_{aniline} < E_{benzene}$$

in case of unsubstituted parent azide, while contradiction occurs in the other two cases so that higher rate of reaction is accompined by higher energy of activation.

In case of acetic acid as a solvent the influence of p-methoxy is reversed from electron releasing group to electron attracting one.

The reactions have been proved to be concerted and not consective ones. This has been proved by trapping any possible intermediate by aniline (cf. page 90).

The mechanism of the reactions studied in different media are all the same as shown by the straight line relationship between $E^{\neq}$ & $\Delta S^{\neq}$ (cf. page 88).

INTRODUCTION

INTRODUCTION

Structure of Azido group.

The chemistry of azides has been the subject of extensive investigations in the last ten years because of its importance in preparative heterocyclic chemistry. Angeli[1] discussed the unsetteled problem whether HN_3 and its derivatives have open-chain formulas HNN:N or ring formula HN:N, the various experimental facts advanced in support of the chain formula. In contrast the ultraviolet absorption spectra of some aryl and aroyl azides in the middle ultraviolet region,[2] for x $C_6H_4N_3$ where x = H, p-Cl, p-Br, p-I, p-OMe, p-NHAC, o-NO_2, m, p-NO_2, o-COOH, m-COOH, H, p-NO_2-$C_6H_4CON_3$, 2,4,6-$Cl_3C_6H_2N_3$ may be support the cyclic structure R-NN:N rather than the open RN:N:N. Lieber et al,[3] studied the infrared spectra of ten organic azides (i.e. Bu, decyl, benzyl, cyclopentyl, phenyl, p-tolyl, p-Bromopheyl, p-nitrophenyl, m-chlorophenyl, and o-chlorophenyl azide to determine the range of frequencies where the strong asymmetric vibration of the azido group was likely to occur. The data show that the N_3 asymmetric vibration is in the region of 2114-2083 cm^{-1} and that it is practically independent of the environmental structure. In the absence of conjugation of an electron acceptor group α-carbon atom the absorption is shifted to 2135-2100 cm^{-}

Measurement of the intensity of this band for 30 azides showed that the intensity is a more sensitive index than band position for structural studies. Electron donor groups raised the intensity & electron acceptor groups lowered it[4].

Azides in Synthetic Chemistry:

Intramolecular cyclization to yield carbazoles, carbolines, phenazines, benzimidazoles, imdazoles, triazoles and related systems have been studied extensively[5]. One can visualize many extensionsto new ring systems. A few limitation have been noted in this reaction, thus in the phenazine synthesis, an alkoxyl group is eliminated in preference to a hydrogen atom whenever both are in the appropriate position for reaction[6,7]. This might indicate some form complexing between imido group and the 2'-alkoxyl group, leading to the elimination. Advantage has been taken of this fact in the selective synthesis. Smith et al[8] found a new reaction for the synthesis of carbezoles consists of cyclization of o-azido, biphenyls by heat or ultraviolet light, a nitro group ortho to the azido group is shown to react in preference to phenyl group resulting in benzfuroxans. Also Smith and Boyer[9] prepared hetero cyclic compounds from aryl azides, carbolines and thienoindole

by preparing the corresponding anilines by diazotization and coupling with sodium azide. Boyer and straw[10] synthesised certain substituted imidazoles from phenyl azide. Yale et al[11] prepared a large number of aliphatic and aromatic heterocyclic acid-hydrazides and their derivatives and related compounds.

Vaughan and Spencer[12] found a new synthesis of 3-substituted 5-hydroxy 1,2,4 oxadiazoles. On treating phenyl azide with CH ≡ CH & $phNHNH_2$ it give 1-aryl-1,2,3-triazoles[13], and substituted 2 phenyl 1,2,3 triazoles respectively. A series of N-sulphonyl methyl urethans, $RSO_2CH_2NHCO_2Et$[14], was prepared by Curtius rearrangement from the corresponding sulphonyl acetyl azides $RSO_2CH_2CO_3$.

Thermolysis or photolysis of vinyl azides gives 1-azirines usually in good yield[15]. Heating ∝-azidostyrene in the gaseous phase produces 2-phenyl-1-azirine.

Method of azide analysis:

Numerous techniques have been developed for the quantitative determination of the number of azido groups per molecule. The problem which must be solved is to release the covalently bound azido group. Most procedures yield one mole of nitrogen per azide leaving the third

nitrogen covalently bonded to the original substrate. Nitrogen evolution is measured by usual gasometric techniques. Arsenite ion has been used[16-19] for azide analysis, but certain difficulties were noted[20] with simple alkyl azides.

Hydrazoic acid thus liberated from some azides can be determined by ceric ion oxidation[21]. An excess of ceric sulphate is added to the hydrazoic acid solution, the excess ceric ion is destroyed

$$2\ Ce^{+4} + 2\ HN_3 \longrightarrow 3\ N_2 + 2\ Ce^{+3} + 2\ H^+$$

with excess potassium iodide, and the iodine is titrated against thiosulphate. This process works only if one can be assured that complete liberation of the azido group has occured.

Water-soluble azides have been treated with hydroiodic acid to obtain quantitative formation of molecular nitrogen and iodine, either of which can be measured[22]. Aryl azides have been handled in the same fashion[23]. These techniques suffer from the difficulty of working with iodine-free hydroiodic acid to yield excess iodine. Sulphonyl azides have been analysed by two processes, release of nitrogen by reaction with triphenyl phosphine, and release of iodine by reaction with potassium iodide-

acetic acid[24]. The best method for most azides seems to be a modification of hydroiodic acid reaction. In this analysis the necessary hydroiodic acid is generated in situ by using a (90%) trichloroacetic acid (10%) water and sodium iodide system. The hydroiodic acid is generated rapidly hence, negligible formation of excess iodine by air oxidation. Excellent results are reported with a broad variety of substrates. Acylazides easily generate one mole of nitrogen per azide[25]. This can be done conveniently on a micro scale with no interference from such groups as nitro, nitroso, azoxy, azo, hydrazo, cyano, amido, imido, amino or ammonium.

Photolysis of Azide

The formation of methylenimine and methyleneime D_3 respectively, presumably from the intermediate CH_3N, CD_3N[26]. Prolonged photolysis in an argon matrix at 4°K produces HNC by the photolysis decomposition of initially formed $CH_2 = NH$[27].

$$CH_3N_3 \xrightarrow[4°K]{h\nu} N_3 + CH_3N \longrightarrow CH_2 = NH \xrightarrow{h\nu} \overset{-}{C} = \overset{+}{N}-H$$

The photolysis of methyl azide has been investigated in the vapour phase at low conversions and various ranges of pressure, temperature, intensity and wavelength[28].

The principal gaseous product was N_2 with small amount of H_2 5-11 % and traces of CH_4, C_2H_4 and C_2H_6. A condensed product as $(CH_3N)_x$ was also found in addition of carbon dioxide, $CH_3-N = N-CH_3$, C_2H_4 indicated the presence of a short chain carried mainly by the CH_3N radical. The heavy product contained 3% of $(CH_2)_6CN_4$ and much larger amounts of other N-containing compounds. The following reactions are suggested.

$$CH_3N_3 \xrightarrow{h\nu} CH_3N + N_2$$

$$CH_3N_3 + CH_3N \longrightarrow (CH_3N)_2 + N_2$$

$$CH_3N^* \longrightarrow H_2 + HCN$$

Irradiation of triarylmethyl azides in hexan solution at room temperature by a low pressure mercury vapor lamp gives the same results, qualitatively as the thermal decomposition[29,30]. The formation of $ph_3C^{\cdot}$ radical in photolysis was demonstrated by its E.S.R spectra[31]

$$Ar_3CN_3 \xrightarrow[h\nu]{\Delta} Ar_3CN \longrightarrow Ar_2C = N-Ar$$

The presence of substituent in any of the three phenyl groups $xC_6H_4(C_6H_5)_2CN_3$ has little effect on the migratory aptitudes in photochemical reactions.

Thermal and photochemical reaction of 1,1-diphenyl ethyl and 2-phenyl-2 propyl azides show-similar, but not entirely regular behavior in the migration aptitudes for