AD

AD 677651

EDGEWOOD ARSENAL
TECHNICAL REPORT

EATR 4218

REARRANGEMENT OF ORGANONITROGEN COMPOUNDS. IMIDE-ISOMIDE EQUILIBRIA

by

Daniel J. Hoy
Edward J. Poziomek

August 1968

DDC
NOV 18 1968

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

Distribution Statement

The information in this document has been cleared for release to the general public; its distribution is unlimited.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when longer needed. Do not return it to the originator.

ACCESSION for
CFSTI WHITE SECTION
DDC BUFF SECTION
UNANNOUNCED
JUSTIFICATION
BY
DISTRIBUTION/AVAILABILITY CODES
DIST. AVAIL. and/or SPECIAL

EDGEWOOD ARSENAL TECHNICAL REPORT

EATR 4218

REARRANGEMENT OF ORGANONITROGEN COMPOUNDS. IMIDE–ISOIMIDE EQUILIBRIA

by

Daniel J. Hoy
Edward J. Poziomek

Defensive Research Department

August 1968

The information in this document has been cleared for release to the general public; its distribution is unlimited.

Task 1B622401A10204

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

The work described in this report was authorized under Task 1B622401A10204, Detection and Warning Investigations (U). This work was started in March 1964 and completed in March 1968. The experimental data are recorded in notebooks 7174, 7279, and 7336.

Reproduction of this document in whole or in part is prohibited except with permission of the Commanding Officer, US Army Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010; however, Defense Documentation Center is authorized to reproduce the document for United States Government purposes.

DIGEST

The purpose of this investigation is to obtain basic information on rearrangements of organonitrogen compounds; specifically studied was the reaction of substituted formamides to yield isocyanides.

Imide–isoimide equilibria were studied by an analysis of the thermal decomposition products of *N*-alkyl(aryl)-*N*-formylacetamides. Relative yields in decarbonylation (arising from imide) vs. isocyanide formation (arising from isoimide) in the pyrolysis of *N*-phenyl, *N*-*n*-butyl, *N*-*sec*-butyl, and *N*-cyclohexyl-*N*-formylacetamides were found to be 99:1, 86:14, 57:43 and 51:49, respectively. Nitriles rather than isocyanides were isolated because of the isomerization which occurs at high temperatures.

It is concluded that the quantities of amide and nitrile isolated may be the net result of a number of reactions: imide–isoimide reversible rearrangement, isoimide α-elimination (possibly reversible), imide decarbonylation (irreversible), isocyanide–nitrile isomerization (irreversible) and imide regeneration from isocyanide and acid through formamide and acetic anhydride. Among the imides studied both an electronic and a steric effect appear to be operating.

CONTENTS

		Page
I.	INTRODUCTION	7
II.	EXPERIMENTAL	8
III.	RESULTS	10
IV.	DISCUSSION	12
V.	CONCLUSIONS	16
	LITERATURE CITED	17
	DISTRIBUTION LIST	19

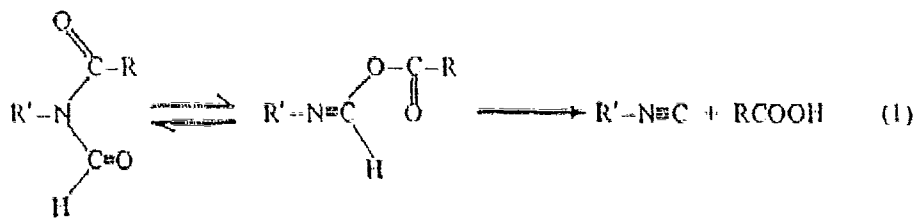
LIST OF TABLES

Table		Page
I.	Products Obtained in the Pyrolysis of *N*-Substituted-*N*-Formylacetamides	11
II.	Relative Reaction Paths in the Pyrolysis of *N*-Substituted-*N*-Formylacetamides	11

REARRANGEMENT OF ORGANONITROGEN COMPOUNDS.
IMIDE – ISOIMIDE EQUILIBRIA.

I. INTRODUCTION.

The formation of isoimides as transient intermediates (which rearrange to the imide or which yield products logically derived from isoimide structures is widely reported.[1-8] Mumm[9] detected an intensive odor of isocyanide in the decarbonylation of *N*-formylbenzanilide but he did not report isolating the product. Similarly, Wheeler[10] claimed that pyrolysis of *N*-formylstearanilide gave phenyl isocyanide and stearic acid but gave no supporting details. Isocyanide production in these reactions gives evidence of an imide–isoimide rearrangement (equation 1).



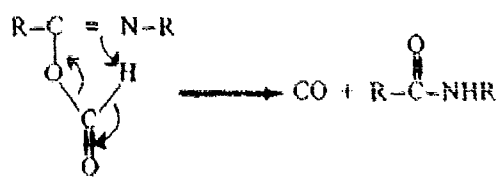
(1)

Isoimides have been isolated only when the function is part of a five-membered ring which also contains a carbon-carbon double bond[11] or when the nitrogen bears a 2,4-dinitrophenyl group.[12 13] These isoimides rearrange via an oxygen-to-nitrogen acyl migration when heated, however the rearrangement observed for the cyclic case may depend on acid or base catalysis.[12]

Mumm and coworkers,[1] postulated a reversible imide–isoimide rearrangement to explain three pyrolysis reactions. Expressing specific examples in general terms, the reactions are pyrolysis of acyclic imides to carboxylic acids and nitriles, pyrolysis of *N*-alkyl(aryl)-*N*-formylamides to the *N*-alkyl(aryl)amides and carbon monoxide, and the pyrolysis of *N*-alkyl(aryl)-*N*-formylamides to isocyanides and carboxylic acids.

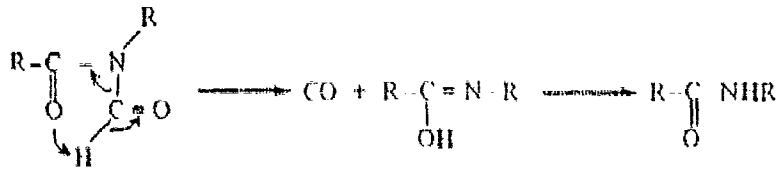
For the pyrolysis of acyclic imides, Sheehan and Corey[5] have written a reversible imide–isoimide rearrangement as a part of the mechanism in agreement with Mumm's postulate. More extensive studies have recently been explained by postulating a concerted mechanism which omits a discrete isoimide intermediate, though the authors consider a path through an isoimide intermidiate as a possible limiting case.[14]

In the pyrolysis of *N*-alkyl(aryl)-*N*-formylamides to *N*-alkyl (aryl)-amides, a decarbonylation mechanism for Mumm's postulated isoimide can be written (equation 2).



(2)

However, decarbonylation could also occur directly from the imide (equation 3).



(3)

For the pyrolysis of *N*-alkyl(aryl)-*N*-formylamides to isocyanides, a mechanism is difficult to write unless prior rearrangement to an isoimide occurs. The isoimide can then undergo an α-elimination (equation 1). The existence of this pyrolysis reaction gives the best evidence for a reversible imide–isoimide equilibrium at high temperatures. In order to investigate Mumm's postulated equilibrium, to determine quantitatively the relative importance of decarbonylation vs. isocyanide formation as pyrolysis pathways, and to investigate the formation of isocyanides from substituted formamides, we studied the pyrolysis of *N*-phenyl-, *N*-*n*-butyl-, *N*-*sec*-butyl- and *N*-cyclohexyl-*N*-formylacetamides.

II. EXPERIMENTAL.

The starting materials were synthesized by acetylating the appropriate formamide derivative with acetyl chloride. The pyrolysis apparatus was a gas chromatograph equipped with a 6 ft x 0.25 in. copper or glass tube in place of the usual column. Sufficient pyrolysis products were then obtained by multiple injection of reactant using a helium carrier gas flow rate of 60 ml/min and oven temperature of 400°. The time of passage through the tube varied between 2 and 25 sec. The combined products were collected at ice-water temperature and separated by preparative glc. The identity of each peak was determined by comparison of its retention time and infra-red spectrum with an authentic sample. Quantitative analyses were obtained with an estimated uncertainty of 3 mole percent by measuring the peak areas with a disc integrator.

Synthesis of *N*-Formylacetanilide

Formanilidine (24.2 gm, 0.02 mole) was dissolved in 250 ml of methylene chloride and cooled in ice. Pyridine (31.7 gm, 0.40 mole) and acetyl chloride (31.4 gm, 0.40 mole) were added and the mixture extracted twice with 100 ml and once with 50 ml portions of water. The methylene chloride solution was dried (Na_2SO_4) overnight, stripped with a rotary evaporator, and distilled with a spinning band column giving 26.0 gm (80%) of the imide: bp 81-82° (0.035 mm) [lit.[10] bp 157-158° (23 mm)]. The product was recrystallized from ether/ligroin; softens 53°; mp 55° (lit.[10] mp 56°).

Synthesis of *N*-(*n*-butyl)-*N*-Formylacetamide

n-Butylformamide (20.2 gm, 0.20 mole) and acetyl chloride (62.7 gm, 0.80 mole) were mixed and stirred at reflux for 5 hr while protected from moisture. After the reaction

solution stood at room temperature for 30 hr, the acetyl chloride was stripped off with a rotary evaporator. The residue was distilled through a spinning band column giving 19.2 gm (67%) of the imide bp 74.5-75.5° (0.70-0.75 mm); n_D^{23} 1.4513.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72, H, 9.15; N, 9.78.

Found: C, 58.9; H, 9.3; N, 9.7.

Synthesis of *N*-(*sec*-butyl)-*N*-Formylacetamide

sec-Butylformamide (20.3 gm, 0.20 mole) was dissolved in 200 ml methylene chloride and pyridine (23.7 gm, 0.30 mole) and acetyl chloride (17.3 gm, 0.22 mole) was added. The solution warmed and turned light yellow upon acetyl chloride addition. It was then cooled in ice and a white salt formed upon complete addition of acetyl chloride. The solution was stirred at room temperature and an additional ten ml of acetyl chloride and five ml of pyridine were added because glc showed an incomplete reaction. The white salt was filtered off and the methylene chloride evaporated whereupon more white salt formed and was filtered off again. The residue was vacuum distilled and gave 22.2 gm (77%) of imide: bp 53.5° (0.10 mm). The product was slightly impure by glc and purified by preparative glc: n_D^{23} 1.4517.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78.

Found: C, 58.5; H, 9.3; N, 9.9.

Synthesis of *N*-Cyclohexyl-*N*-Formylacetamide

Cyclohexylformamide (25.5 gm, 0.20 mole) was dissolved in 250 ml of methylene chloride and pyridine (31.7 gm, 0.40 mole) and acetyl chloride (31.4 gm, 0.40 mole) was slowly added with ice cooling. A white salt formed immediately, the mixture turned light yellow and was allowed to stand for one hour. The mixture was poured into a separatory funnel and washed with three 100 ml portions of water. The methylene chloride solution was dried (Na_2SO_4), stripped of solvent, and distilled through a spinning band column giving 23.2 gm (68%) of imide: bp 74-75° (0.20 mm); n_D^{23} 1.4872.

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88, H, 8.94; N, 8.28.

Found: C, 63.8; H, 9.0; N, 8.3.

Pyrolysis

The weight of the injected imide may be as much as ~5% low due to evaporation from the needle. The corrected weights are subject to the ~3% uncertainty of the glc analysis.

Pyrolysis of *N*-Formylacetanilide

White crystals formed in the collector bottle: mp 109-113° without purification (acetanilide: mp 113-115°). The collector bottle was washed with a small quantity of chloroform. An infra-red spectrum of the chloroform solution showed a small peak at 4.48 μ, identical with the nitrile peak at 4.48 μ of an authentic benzonitrile sample. A glc of the chloroform solution (column: 30% SE 30 on 45/60 Chrom. W; 3/8 in. x 20 ft) gave a peak with a retention time identical to that of benzonitrile.

Pyrolysis of *N*-(*n*-Butyl)-*N*-Formylacetamide

Copper Tube

The imide (228 mg, 1.59 mmole) was injected in 50 μl aliquots. The products (186 mg) were collected in ice and analyzed by glc (column: 30% SE 30 on 45/60 Chrom. W; 3/8 in. x 20 ft). Product weight corrected for carbon monoxide loss from 85% of the starting material is 224 mg.

Glass Tube

The imide (228 mg, 1.59 mmole) was injected in 50 μl aliquots. The products (195.5 mg) were collected in ice and analyzed by glc (column: 30% SE 30 on 45/60 Chrom. W; 3/8 in. x 20 ft). Product weight corrected for carbon monoxide loss from 85% of the starting material is 234 mg.

Pyrolysis of *N*-(*sec*-Butyl)-*N*-Formylacetamide

The imide (461 mg, 3.22 mmole) was injected in 45 μl aliquots. The products (433 mg) were collected in ice and analyzed by glc (column: 30% SE 30 on 45/60 Chrom. W; 3/8 in. x 20 ft). The product weight corrected for carbon monoxide loss with 33% unreacted starting material and 57% of the reacted imide decarbonylating is 467 mg.

Pyrolysis of *N*-Cyclohexyl-*N*-Formylacetamide

The imide (980 mg, 5.80 mmole) was injected in 45 μl aliquots. The products (892 mg) were collected in ice and analyzed by glc (column: 30% SE 30 on 45/60 Chrom. W; 3/8 in. x 20 ft). The weight corrected for carbon monoxide loss with 8% unreacted starting material and 51% of the reacted imide decarbonylating is 880 mg.

III. RESULTS.

Starting materials were synthesized by acetylating the appropriate formamide derivative with acetyl chloride. The *N*-formylacetamides were pyrolyzed by passing them through copper or glass tubes at 400°. Experimental results are summarized in tables I and II.

Table I. Products Obtained in the Pyrolysis of *N*-Substituted-*N*-Formylacetamides

Nitrogen Substituent	Acetamide (% yield)	Nitrile (% yield)	Acetic Acid (% yield)
Phenyl[a]	> 99	< 1	–
n-Butyl[a]	75	12	13
n-Butyl[b]	74	10	16
sec-Butyl[a]	40	30	30
Cyclohexyl[a]	34	35	31

[a]copper tube, [b]glass tube

Table II. Relative Reaction Paths in the Pyrolysis of *N*-Substituted-*N*-Formylacetamides

Nitrogen Substituent	% Decarbonylation	% Isonitrile–Acid
Phenyl	>99	< 1
n-Butyl	86	14
sec-Butyl	57	43
Cyclohexyl	51	49

Further investigation of the *N*-*n*-butyl-*N*-formylacetamide pyrolysis reaction was performed by running a variety of reactions on degassed reactants in sealed tubes. Equations 4–8 record the observed products analyzed for by glc along with the time and temperature of the reaction.

$$n\text{-}C_4H_9NHCHO \xrightarrow[30\ \text{min}]{380^\circ} \text{No Reaction} \quad (4)$$

$$n\text{-}C_4H_9N(COCH_3)CHO \xrightarrow[30\ \text{min}]{365^\circ} n\text{-}C_4H_9NHCOCH_3 + \text{high pressure (CO)} \quad (5)$$

$$n\text{-}C_4H_9NC + CH_3COOH \xrightarrow[30\ \text{min}]{325^\circ} n\text{-}C_4H_9NHCOCH_3\ (80\%) + n\text{-}C_4H_9CN\ (10\%) + n\text{-}C_4H_9NHCHO\ (10\%) \quad (6)$$

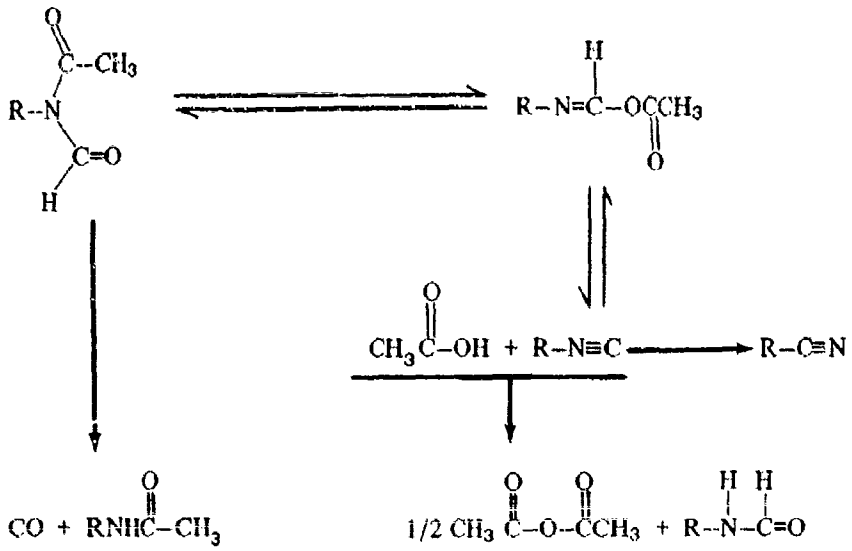
$$n\text{-}C_4H_9NC \xrightarrow[15\ \text{min}]{310^\circ} n\text{-}C_4H_9CN \qquad (7)$$

$$n\text{-}C_4H_9NHCHO + (CH_3CO)_2O \xrightarrow[30\ \text{min}]{350^\circ} n\text{-}C_4H_9NHCOCH_3(50\%) + CH_3COOH(50\%) \qquad (8)$$
$$+ \text{high pressure (CO)}$$

If the reaction represented in equation 5 is not run to completion, the odor of isocyanide is detectable upon opening the tube.

IV. DISCUSSION.

The results are conveniently discussed in terms of reaction scheme I. Although the experimental information required to fulfill the necessary conditions for unimolecular reaction



Scheme I. The Imide-Isoimide Rearrangement.

mechanisms[16] has not been determined, we postulate that the decarbonylation and the α-elimination (isocyanide formation) reactions are unimolecular. The agreement within experimental error of the results for pyrolysis of the *n*-butyl derivative in both the copper and glass tube supports the conclusion that the reactions whose rates determine the product ratios are homogeneous.

The quantities of amide and nitrile isolated may be the net result of a number of possible reactions: imide–isoimide reversible rearrangement, isoimide α-elimination (possibly reversible), imide decarbonylation (irreversible), isocyanide–nitrile isomerization (irreversible) and imide regeneration from isocyanide and acid through formamide and acetic anhydride.

Though all these rates and their dependence upon the R group is not known, an explanation of the general features of the R-group influence upon reaction pathway can be proposed which seems logical in view of already determined isocyanide isomerization rates[16-18] and the electronic and steric effects of the R-groups.

The thermal unimolecular isomerization of isocyanides to nitriles explains the presence of the nitriles as the products of the pyrolysis.[16-18] Several of the isocyanides in this study were so completely isomerized under the exact conditions of imide pyrolysis their odor was barely detectable in the nitrile product. Furthermore, isomerization rate constants can be estimated for the isocyanides by using the Arrhenius parameters for methyl isocyanide reported by Schneider and Rabinovitch[16] and the influence of the nitrogen substituent on the isomerization rate reported by Casanova, et al.[18] Thus an estimated lower limit is $k = 5$ sec^{-1}, a number sufficiently large to explain the exclusive isolation of nitrile.

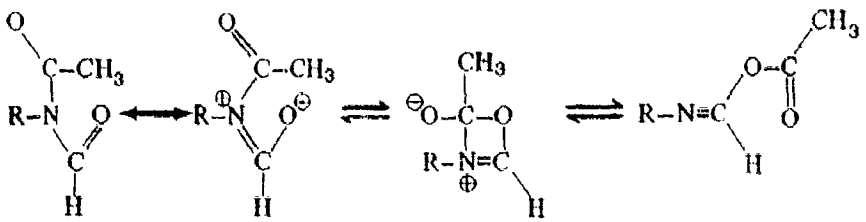
Rabinovitch and Kohlmaier[17] determined the *p*-tolyl isocyanide gas phase isomerization rate to be 75×10^{-5} sec^{-1} at 200°. Casanova, et al.,[18] showed phenyl isocyanide isomerization rates in diglyme to be only slightly dependent upon a *para* substituent, suggesting the gas phase isomerization rate of phenyl isocyanide is probably very similar to that of *p*-tolyl isocyanide. They also determined the ethyl and *sec*-butyl isocyanide gas phase isomerization rates to be 10.4×10^{-5} sec^{-1} and 3.45×10^{-5} sec^{-1} respectively at 200°. Thus comparison of gas phase isomerization rate constants gives the order: phenyl $\gg$ *n*-alkyl $>$ *sec*-alkyl. Since the rate of nitrile formation relative to the rate of decarbonylation is *sec*-alkyl $>$ *n*-alkyl $>$ phenyl for imide pyrolysis, this order is achieved in spite of the order of isocyanide isomerization rates.

Isomerization to nitrile may not be the only reaction of the isocyanide formed. The isocyanide and acid may revert to imide if the α-elimination is a reversible reaction or if a second pathway through formamide and acetic anhydride[19] is operative (equation 9). If imide originally decomposing to isocyanide and acid does re-form and then decarbonylates, the nitrile isolated would be less than would be the case if the exclusive isocyanide reaction were isomerization. Sealed tube reactions (equations 6 and 8) show that either one or both of these reaction sequences can form imide and could be present in the flow method pyrolysis.

$$R{-}N{\equiv}C + CH_3COOH \xrightarrow{+CH_3COOH} R{-}\overset{H}{\overset{|}{N}}{-}CHO + (CH_3CO)_2O \xrightarrow{-CH_3COOH} R{-}N\begin{matrix} COCH_3 \\ CHO \end{matrix} \qquad (9)$$

Failure to pyrolyze the imides under conditions that allow isocyanide isomerization to favorably compete with other isocyanide reactions may give results which differ from the flow method and even mask the isocyanide–acid mode of decomposition. Thus the higher pressures obtained by pyrolysis in a sealed tube may so enhance the re-formation of imide that decarbonylation is the only net reaction observed (note equation 5). Heating the imide to a temperature near its boiling point at atmospheric pressure yielded a solution which darkened rapidly, evolved a gas, and possessed an isocyanide odor. Knowledge of the reactions possible for a solution of the parent imide, its corresponding amide and formamide, isocyanide, nitrile, acetic acid, and acetic anhydride between 100° and 200° discouraged further investigation.

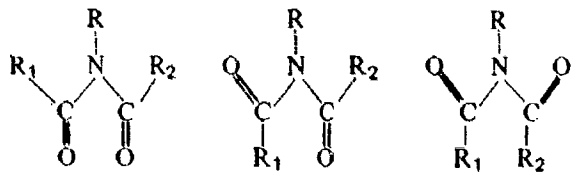
A mechanism for the formation of nitrile and carboxylic acid from the imide is difficult to conceive without the isoimide α-elimination and the isocyanide somerization. The four-centered cyclic transition state for the reversible imide > isoimide rearrangement is that proposed by Curtin and Miller[12] (equation 10).



imide transition state isoimide (10)

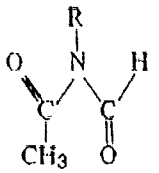
Among the imides studied, both electronic and steric effects seem to be operating. An electronic effect seems best able to explain the results for the phenyl imide. The electron density of the nitrogen atom can promote the imide's ability to achieve the transition state as shown by the resonance form written. For the phenyl imide, the nitrogen electron density is significantly decreased in comparison to the alkyl imides by electron delocalization into the benzene ring. We suggest this is the reason for the much smaller nitrile:amide ratio for the phenyl imide as compared to the alkyl imides. The same nitrogen electron density argument, now based on the inductive effect crucially influencing the imide to isoimide isomerization rate, could be a factor increasing the nitrile:amide ratio as one goes from the primary to secondary alkyl groups. However, the sterically preferred imide conformation may be more influential.

The trend of the sterically preferred imide conformer with the change in R-group from primary to secondary at the pyrolysis temperature can be deduced from imide and amide conformation determinations at room temperature. The rotational barrier of the amide bond leads to three possible conformers for an imide, viz,

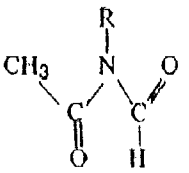


A B C

Dipole moment data support assignment of conformation B to *N*-methyldiformamide, diacetamide and *N*-methyldiacetamide.[20] Though not determined it is likely that the B conformation (I or II) can be assigned to the imides of this study.



I



II

Monosubstituted formamides are predominantly *trans* and show a small trend towards the *cis*-conformer with increasingly bulky substituents.[21] In unsymmetrical disubstituted formamides, the formyl hydrogen is *cis* to the bulkier substituent.[22] Although the amide bond will no longer show *cis-trans* isomerism at the temperature of this pyrolysis,[23] the steric considerations can still be used to deduce the trend of conformation with R-group. Thus as one goes from a primary to a secondary alkyl group, the trend will be for the formyl and the acetyl to maintain a more *trans*-like character even though rotation may occur for both groups. This is precisely the trend in conformation favorable for producing a trend towards rearrangement to an isoformimide. As the trend in nitrile:amide ratio agrees with the trend favoring isoformimide formation, rearrangement to isoformimide appears to be the rate determining step for degradation to nitrile and acid.

As first discussed in the introduction, a unimolecular mechanism for decarbonylation can be written from either the imide or isoimide. The considerations used to explain the changing nitrile:amide ratio with R-group imply the imide → isoformimide rearrangement is the rate determining step in nitrile formation. In view of this fact, it is tempting to try to exclude the possibility of an isoacetimide in the decarbonylation mechanism by using an argument based on the electronic or steric effects influencing the relative rate of isomerization of any single imide to either the isoformimide or isoacetimide. Specifically, for the phenyl imide, the nitrile:amide ratio was much smaller than for alkyl imides because the lower electron density on nitrogen is unfavorable for rearrangement to the isoformimide. One would thus expect rearrangement to the isoacetimide to also be unfavorable. Because decarbonylation is rapid in comparison to nitrile formation, one is tempted to exclude the isoacetimide as a decarbonylation intermediate in favor of the alternative mechanism. For the alkyl imides, the favored conformer, especially for the secondary alkyl groups, has a *trans*-like acetyl. Both decarbonylation mechanisms require the unfavored *cis*-like conformer. In spite of this, decarbonylation is more rapid than nitrile formation through the isoformimide. Thus one is again tempted to favor exclusion of the isoacetimide from the decarbonylation pathway. However, there are two reasons why the considerations valid for explaining the change in nitrile:amide ratio between two different imides are not valid for explaining the ratio for a single imide. The first is that imide re-formation reactions competing with isocyanide isomerization may prevent the nitrile:amide ratio from representing the relative rates by which the imide forms isoformimide or decarbonylates. The second is that the activation energy for the rearrangement to isoformimide and isoacetimide may be significantly different.

V. CONCLUSIONS.

It is concluded that the quantities of amide and nitrile isolated may be the net result of a number of reactions: imide–isoimide reversible rearrangement, isoimide α-elimination (possibly reversible), imide decarbonylation (irreversible), isocyanide–nitrile isomerization (irreversible) and imide regeneration from isocyanide and acid through formamide and acetic anhydride. Among the imides studied, both an electronic and a steric effect appear to be operating.

LITERATURE CITED

1. O. Mumm, H. Hesse, and H. Volquartz. Berichte der Deutschen Chemischen Gesellschaft 48, 379 (1915).

2. F. Cramer and K. Baer. Chem. Ber. 93, 1231 (1960).

3. C. L. Stevens and M. E. Munk. J. Amer. Chem. Soc. 80, 4065 (1958).

4. H. H. Wasserman and M. B. Floyd. Tetrahedron Supplement No. 7, 441 (1966).

5. J. C. Sheehan and E. J. Corey, J. Amer. Chem. Soc. 74, 4555 (1952).

6. C. G. Overberger and E. Sarlo. J. Amer. Chem. Soc. 85, 2446 (1963).

7. D. S. Kemp. Tetrahedron 23, 2001 (1967).

8. A. Kornhauser and D. Keglevic. Tetrahedron 18, 7 (1962).

9. O. Mumm. Berichte der Deutschen Chemischen Gesellschaft 43, 886 (1910).

10. H. L. Wheeler. Amer. Chem. J. 18, 695 (1896).

11. W. R. Roderick and P. L. Bhatia. J. Org. Chem. 28, 2018 (1963).

12. D. Y. Curtin and L. L. Miller. Tetrahedron Letters 23, 1869 (1965).

13. T. Shono, M. Kimura, Y. Ito, K. Nishida, and R. Oda. Bull. Chem. Soc. Japan 37, 635 (1964) The authors claim preparation of several isoimides based on the position of infra-red absorption bands. This is not conclusive evidence for the isoimide structure.

14. W. S. Durrell, J. A. Young, and R. D. Dresdner. J. Org. Chem. 28, 831 (1963).

15. A. Maccoll in "Advances in Physical Organic Chemistry," Vol. 3. p 96. V. Gold, Ed., Academic Press, London. 1965.

16. F. W. Schneider and B. S. Rabinovitch. J. Amer. Chem. Soc. 84, 4215 (1962).

17. B. S. Rabinovitch and G. Kohlmaier. J. Phys. Chem. 63, 1793 (1959).

18. J. Casanova, Jr., N. D. Werner, and R. E. Schuster. J. Org. Chem. 31, 3473 (1966).

19. A. Gautier. Annales Chimie e de Physique 17, 224 (1869).

20. C. M. Lee and W. D. Kumler. J. Amer. Chem. Soc. 84, 571 (1962).

21. L. A. LaPlanche and M. T. Rogers. J. Amer. Chem. Soc. 86, 337 (1964).

22. L. A. LaPlanche and M. T. Rogers. J. Amer. Chem. Soc. 85, 3728 (1963).

23. R. C. Neuman, Jr., and L. B. Young. J. Phys. Chem. 69, 2570 (1965).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
CO, Edgewood Arsenal
ATTN: SMUEA-RPRE
Edgewood Arsenal, Maryland 21010

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP
NA

3. REPORT TITLE
REARRANGEMENT OF ORGANONITROGEN COMPOUNDS. IMIDE - ISOIMIDE EQUILIBRIA (U)

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
This work was started in March 1964 and completed in March 1968

5. AUTHOR(S) (First name, middle initial, last name)
Hoy, Daniel J. and Poziomek, Edward J.

6. REPORT DATE
August 1968

7a. TOTAL NO. OF PAGES
24

7b. NO. OF REFS
23

8a. CONTRACT OR GRANT NO.
(16) Proj. D/A-1-B-622401-A-102-
(17) Task 1-B-622401-A-10204

b. PROJECT NO.

c. Task No. 1B622401A10204

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
EATR 4218

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
The information in this document has been cleared for release to the general public; its distribution is unlimited.

11. SUPPLEMENTARY NOTES
Detection and Warning Investigations (U)

12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

(U) The purpose of this investigation is to obtain basic information on rearrangements of organonitrogen compounds; specifically studied was the reaction of substituted formamides to yield isocyanides. Imide-isoimide equilibria were studied by an analysis of the thermal decomposition products of N-alkyl(aryl)-N-formylacetamides. Relative yields in decarbonylation (arising from imide) vs isocyanide formation (arising from isoimide) in the pyrolysis of N-phenyl, N-n-butyl, N-sec-butyl, and N-cyclohexyl-N-formylacetamides were found to be 99:1, 86:14, 57:43 and 51:49, respectively. Nitriles rather than isocyanides were isolated because of the isomerization which occurs at high temperatures. It is concluded that the quantities of amide and nitrile isolated may be the net result of a number of reactions: imide-isoimide reversible rearrangement, isoimide α,β-elimination (possibly reversible), imide decarbonylation (irreversible), isocyanide-nitrile isomerization (irreversible) and imide regeneration from isocyanide and acid through formamide and acetic anhydride. Among the imides studied both an electronic and a steric effect appear to be operating.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Organonitrogen compounds						
Imide						
Isoimide						
Isocyanide						
Isonitrile						
Pyrolysis						
Formamides						
Acetamide						
Formylacetamide						
Alpha-Elimination						
Nitrile						
Decarbonylation						

UNCLASSIFIED

Security Classification