WORK

EMBODIED IN THE

II. SC. THESIS
**INTRODUCTION**

**REFERENCE OF THE WORK EMBODIED IN THE**

**M. SC. THESIS**

The thesis entitled

"A study in the reactivity of the hydrogen atom of the imido (−NH−) group situated between two keto groups"

presented to the University of Bombay in 1941 and for which the degree of M. Sc. was awarded to the candidate,

comprised of:

(I) Mercuration of the substituted amides of acetyl urethane using mercury acetamide,

(II) Interaction of sodamide with the substituted amides of acetyl urethane, and

(III) A study in the velocity of interaction of phenyl hydrazine with the mercury derivatives of acetyl urethane and its substituted amides.

The reactivity of the hydrogen atom of the imido (−NH−) group situated between two keto groups or between any two electrophilic groups was studied in comparison with that of the methylene group situated between two such groups. The former grouping is present in acetyl urethane,
CH₃CO,III,COOH₂, and its substituted amides having the

general formula:

CH₃CO,III,CO,NHR

(where R is an alkyl or an aryl radical), whereas the latter
is found to be present in acetooacetic ester, CH₃COCH₂COOH₂, and its substituted amides possessing the following structure:

CH₃CO.CH₂.CO,NHR

With this end in view, the action of (i) mercury
acetamide and (ii) sodamide on acetyl urethane and its
substituted amides was investigated. Shah (J. Ind. Chem. Soc.,
1936, 15, 149) obtained mercury derivatives of acetyl urethane
and some of its aromatic substituted amides. This work was
continued further and some more aromatic and aliphatic
substituted amides of acetyl urethane were employed.

The general constitution assigned to the mercury
derivatives of the substituted amides of acetyl urethane is:

\[ \text{CH}_3\text{CO} \quad \text{CO.CH}_3 \]

\[ \text{H} \quad \text{Hg} \quad \text{H} \]

\[ \text{H}_2\text{N} \quad \text{CO} \quad \text{CO.NHR} \]

where R may be a methyl, ethyl, phenyl, tolyl, etc. group.
The action of mercury acetamide on the following substituted amides of acetyl urethane had been studied:

1. Acetyl methyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_3 \)
2. Acetyl ethyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_2\text{H}_3 \)
3. Acetyl propyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_3\text{H}_7 \)
4. Acetyl isopropyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_3\text{H}_7 \)
5. Acetyl 1:4:5-xylyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_6\text{H}_3(\text{CH}_3)_2 \)
6. Acetyl o-anisidyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NHCH}_5\text{H}_4\text{OCH}_3 \)
7. Acetyl o-phenoxydyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NH.C}_6\text{H}_4\text{OC}_2\text{H}_5 \)
8. Acetyl p-phenoxydyl carbamido: \( \text{CH}_3\text{CO.NH.CO.NH.C}_6\text{H}_4\text{OC}_2\text{H}_5 \)

By mixing hot alcoholic solutions of the respective amides and mercury acetamide, and heating the mixture under a reflux condenser, the mercury compounds were obtained as amorphous powders.

These compounds are immediately decomposed by dilute hydrochloric acid, hydrogen sulphide, sodium sulphide and ammonium sulphide, the corresponding mercury salts being formed. With potassium iodide, the following reaction occurs:

\[ (\text{CH}_3\text{CO.NH.CO.NHHR})_2\text{Hg} + 4\text{KI} \rightarrow 2\text{KIN} + \text{H}_2\text{O} \]

\[ \rightarrow 3\text{CH}_3\text{CO.NH.CO.NHHR} + 2\text{KIN} + \text{K}_2\text{H}_2\text{I}_4 \]
Hydrazylamine, hydrazine hydrate and phenyl hydrazine immediately decompose all the mercury compounds liberating metallic mercury.

The reaction of these mercury compounds with phenyl hydrazine appeared to be complicated and could not be expressed in a simple manner, because considerable amounts of mercury diphenyl were also produced during the reaction. Besides this, benzene and the corresponding amine were also produced in small quantities. While studying the action of phenyl hydrazine on these mercury compounds, it was observed that the reaction rate was not the same in all the cases.

Hence the rate of decomposition of various mercury compounds with phenyl hydrazine was studied by measuring the rate of evolution of nitrogen gas. The difference in these velocities was attributed to different substituent groups of the mercury compounds.

All the above-mentioned properties of the mercury compounds indicate the presence of a very weak N-Hg bond.

Andreozzi (Bot., 1892, 5, 689) reported that when acetyl urethane was dissolved in absolute ether and pieces
of freshly-cut metallic sodium were put into it, and if the mixture was kept for twenty-four hours, a white compound settled at the bottom of the flask, which on interaction with methyl iodide, gave methyl acetyl urethane:

\[ \text{CH}_3\text{CO}_2\text{H(CH}_3\text{)}\cdot\text{COOCH}_2\text{H}_5 \]

Shah and Itakhaporia (J. Chem. Soc. Trans., 1936, 451) also prepared the sodium derivative of acetyl urethane. The white sodium compound was directly condensed with benzanilido imidochloride. Shah and Ghodiwalla (23rd Ind. Sci. Congress, Vol. 2, 1936, 184) prepared the sodium derivative of N-phenyl urethane by a similar method and directly condensed it with benzanilido imidochloride. But these chemists had not isolated the sodium derivatives.

It is true that the method of introducing sodium or potassium into organic compounds by the direct action of the respective metals in an inert solvent is of wide application. But the use of sodamide for the preparation of sodium derivatives of organic compounds has proved to be of much wider application. Since the substituted amides of acetyl urethane were very sparingly soluble in ether,
metallic sodium was not effective in producing their sodium derivatives. Sodium was therefore employed for their preparation. The action of sodium on the following substituted amides of acetyl urethane was studied:

1. Acetyl urethane, $\text{CH}_3\text{CO}_2\text{H}$
2. Acetyl phenyl carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4$.
3. Acetyl m-tolyl carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OH}$.
4. Acetyl p-tolyl carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OH}$.
5. Acetyl p-anisidyld carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OC}_6\text{H}_5$.
6. Acetyl $\alpha$-naphthyl carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OH}$.
7. Acetyl $\beta$-naphthyl carbamido, $\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OH}$.
8. Phenyl urethane, $\text{C}_6\text{H}_5\text{CO}_2\text{H}_2\text{H}_4$.

The amides from (1) to (7) produced mono-sodium derivatives of the general constitution:

$$\text{CH}_3\text{CO}_2\text{H}_2\text{CO}_3\text{H}_4\text{H}_2\text{OH}$$

where R is a phenyl, tolyl, anisidyl, etc. group. Phenyl urethane also yielded a mono-sodium derivative.

The freshly prepared sodium compounds were all white.
in colour. They are hygroscopic and are sensitive to moisture. All the compounds are quantitatively decomposed by water and dilute hydrochloric acid, with the formation of the original amide and caustic soda in the first case and the original amide and sodium chloride in the latter case.

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