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IV. The Degenerate Bimolecular Exchange
of Protons in Ketimines

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IV. The Degenerate Bimolecular Exchange of Protons in Ketimines¹,²

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The imine protons of nitrogen-15 labeled ketimines exhibit temperature-dependent nuclear magnetic resonances. Analysis of the effect of concentration of substrate on the mean lifetime indicates that the spectral changes result from a bimolecular exchange of protons between imines. The activation energy of this process in
diphenylketimine-$^{15}$N was determined to be 13.8 ± 2 kcal./mole, whereas in s-butylphenylketimine-$^{15}$N, the activation energy was about 6 kcal./mole. In the latter case, separate resonances were observed for the distinct syn and anti isomers.

**Introduction**

Nuclear magnetic resonance spectroscopy is ideally suited for rate studies of rapidly reversible unimolecular reactions with Arrhenius activation energies between 5 and 20 kcal./mole. Isomerization processes, ring inversions, and valence tautomizations have been studied by analysis of the temperature variation

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of spectral parameters. Reactions of higher order involving proton transfers have also been examined by means of spectral changes as a function of solvent, pH, and solute concentration. \(^{11}\) The rapid rates of proton transfer reactions have often caused the spectral lineshapes to be temperature insensitive. \(^{12}\) Reversible changes with temperature in the spectra of nitrogen-15 labeled ketimines are interpreted in the following discussion in terms of an intermolecular exchange of protons between nitrogen atoms.

**Results and Discussion**

In the absence of exchange, the proton on nitrogen in diphenyl-ketimine-\(^{15}\)N (I) should be a doublet because of coupling with nitrogen-

\[
\begin{align*}
\text{C}_6\text{H}_5 & \text{C} & \text{C}_6\text{H}_5 \\
\text{H} & & \text{H} \\
\text{N}^{15} & & \\
\end{align*}
\]

15. At 40°, however, the imine hydrogen resonance varies from a
single sharp peak in carbon disulfide or a broad singlet in carbon tetrachloride and dimethyl sulfoxide, to no observable peak at all in acetonitrile, deuterochloroform, and pentane. The spectrum of the ketimine in 2-5% solutions of the last three solvents was examined to -50°, at which temperature the solutions solidified. Whereas no change occurred over this temperature range for the acetonitrile and deuterochloroform solutions, the expected doublet appeared below 0° in the spectrum of the pentane solution (Figures 1a, b and 2). Under

(13) The pentane had been treated with sulfuric acid for 2 days, distilled, and dried over calcium hydride. The field increases from left to right on all spectra.

identical conditions of solvent and temperature, the nitrogen-14 compound exhibited a single broad imine resonance which fell midway between the two peaks of the nitrogen-15 compound (Figure 1c). The integrated intensity of the two peaks, furthermore, was 1/10 that of the phenyl peaks. There remains little doubt, therefore, that the doublet resonance ($J_{15\text{NH}} = 51.2$ c.p.s.) arises from the imine proton coupled with nitrogen-15.

This same phenomenon was observed at lower temperatures in the spectrum of s-butylphenylketimine-15N (II). At -60°, the imine proton resonance consists of four peaks, which must arise from the two distinct ketimine isomers (IIa and b) which are possible in this
unsymmetrical system (Figure 3). The components of each small doublet are chemically shifted about 11 c.p.s. from each other. The low-field components in each doublet are separated by 50.6 c.p.s., and the high-field components are separated by 50.9 c.p.s. As the temperature of the pentane solution is raised, the components of each doublet broaden and finally coalesce (Figure 4, left side; only one of the doublets is shown). The free-energy difference between isomers was calculated to be 70 cal./mole from the equilibrium constant at \(-60^\circ\) (1.5, obtained by electronic integration).

The observation of separate geometric isomers of N-substituted imines has been claimed erroneously in the past.\(^\text{14,15}\) The

\(^{14}\) Oximes, semicarbazones, and N-haloimines are excluded from consideration in this context.


benzophenone imines. The present observation of separate resonances for the two isomers of \( \text{\textit{s}} \)-butylphenylketimine-\( ^{15} \text{N} \) is the first example of \textit{cis-trans} isomerism about a carbon-nitrogen double bond which is unsubstituted at nitrogen.

The coalescence of the peaks for the two isomers (Figure 4) results from a simple spin-exchange phenomenon. The possible mechanisms of exchange will be discussed in detail for the case of the unsymmetrical imine II.

\[
\begin{align*}
\text{A.} & \quad \text{IIa} \quad \text{IIb} \\
\text{B.} & \quad \text{M} + \text{SH} \quad \text{protonation or deprotonation} \\
\text{C.} & \quad \text{M} + \text{M'} \quad \text{M'} + \text{M} \\
\text{D.} & \quad \text{D} \quad \text{D'}
\end{align*}
\]

Mechanism A involves a \textit{cis-trans} isomerization. Mechanism B involves a proton exchange between monomer and some other species such as water or ammonia. Mechanism C is a special case of B, in which the second species is also monomer. Mechanism D involves a proton exchange within a dimeric structure.

In order to differentiate between the various mechanistic possibilities, the Gutowsky-Holm method\(^5,\)\(^18\) was employed to determine

(18) The author is indebted to Dr. S. Borčić for making available a Fortran program for calculation of line shapes as a function of the mean lifetime. The values of \( \tau \) were determined by direct
comparison of observed and calculated spectra (Figure 4).

mean lifetimes, \( \tau \), which are related to the reaction rate in a manner.

(19) The mean lifetime, \( \tau \), is defined as the time required for all but \( 1/e \) of the molecules to have reacted.

to be discussed. Figure 4 compares the calculated spectra with the observed spectra for various temperatures. The molecularity of the reaction must be determined before rates may be calculated from the mean lifetime.

Certain mechanistic possibilities may be eliminated by observing the effect on the mean lifetime of changes in reaction conditions. Addition of water directly to the solution of pentane had no effect on the mean lifetime. The presence of calcium hydride or calcium oxide in the n.m.r. tube had a similarly negligible effect. Mechanism B is thus eliminated, since addition or destruction of the most likely choices for \( \text{SH} \), water and ammonia, do not affect the rate. When the concentration of ketimine was varied, however, significant changes in the mean lifetime were indicated by substantial line-shape changes. This excludes as the only mechanism any kind of unimolecular process, such as those represented in mechanisms A and D. Mechanism C therefore best accounts for the experimental details:

\[
\begin{align*}
\text{H} & \text{N} \quad + \quad \text{H}^* \text{N}^* \quad \xrightarrow{\text{R}} \quad \text{H}^* \text{N} \quad + \quad \text{H} \text{N}^* \\
\text{R} \text{C} \text{R} & \quad + \quad \text{R} \text{C} \text{R} & \quad \xrightarrow{\text{R}} \quad \text{R} \text{C} \text{R} & \quad + \quad \text{R} \text{C} \text{R}
\end{align*}
\]
Such a pathway is bimolecular and degenerate; not only are both reactants the same, but they are the same as the products.

Although the mechanism has been discussed in terms of a bimolecular process, the actual molecularity remains to be determined. The experimental facts could also be interpreted in terms of a termolecular process. The Gutowsky-Holm-Borčić treatment enables one to determine the mean lifetime, \( \tau \), which is simply the reciprocal of the first-order rate constant for a unimolecular process. The relationship is more complicated for reactions of higher order.

The integrated form of the rate law given in

\[
- \frac{dM}{dt} = kM^n
\]

Equation 1 is:

\[
\frac{M_0/e}{M_0} = \tau = \int \frac{M^{-n} dM}{M_0} = \int k \, dt
\]

For \( n = 1 \):

\[
k\tau = \ln \frac{M_0}{M_0/e} = \ln e = 1
\]

In general, for \( n \neq 1 \):

\[
k\tau = - \left[ \frac{1}{-n + 1} \frac{M^{-n+1}}{M_0} \right] \frac{M_0/e}{M_0}
\]

\[
= \frac{1}{1 - n} \left[ M_0^{1-n} - \left( \frac{M_0}{e} \right)^{1-n} \right]
\]

\[
= M_0^{1-n} \left( 1 - \frac{e^{n-1}}{1 - n} \right)
\]
Thus, \[ \log \tau = (1 - n) \log M_0 - \log k' \] (3)

where \[ \frac{1}{k'} = \frac{1}{k} \left( \frac{1 - e^{n-1}}{1 - n} \right) = \tau M_0 n^{-1} \]

A statistical factor of 2, which arises because two equivalent protons are exchanged in each reaction, is canceled by the spin factor which arises because exchange between nuclei of the same spin is not observed in the n.m.r. experiment. From the slope of a plot of log \( \tau \) vs. log \( M_0 \), after equation 3, the molecularity was calculated to be about 1.7. Since the error in measuring the values of \( \tau \) from calculated spectra is at least 10%, and the error in \( M_0 \) is relatively large, this plot was deceptively linear, and the result must be judged accordingly. This analysis at least casts serious doubt on the presence of higher-order processes. A second-order process is most suitably accommodated by a transition state involving a concerted shift of two protons in a four-membered ring:

![Diagram of a four-membered ring transition state](image)

An admixture of a unimolecular process such as mechanism D cannot be excluded.

Arrhenius plots for the exchange reactions of I and II may be constructed from the rate constants calculated by equation 2 from machine-determined values of \( \tau \) (Figures 5 and 6). The activation energy for the degenerate proton exchange in diphenylketimine is thus
calculated to be $13.8 \pm 2$ kcal./mole, and the values for $\beta$-butylphenylketimine are 6.5 and $6.6 \pm 2$ kcal./mole. Two values arise since approach to the transition state can occur from either direction. The smaller value is necessarily associated with the less stable isomer. No imine hydrogen resonance was observed down to $-80^\circ$ for di-$n$-butylketimine-$^{15}N$. The activation energy for exchange in systems containing two aliphatic substituents is therefore probably less than 5-7 kcal./mole. Sensitivity and solubility problems prevented accurate concentration studies of the proton exchange in I. It should be noted that the calculation of activation energies is completely independent of both the molecularity and the units of concentration, since changes in these quantities will not affect the slope of the plot. Therefore, the activation parameters are valid, even if the proposed mechanism of spin exchange is incorrect.

An isomerization process such as that depicted by mechanism A has been studied by Andreades$^{20}$ for the N-substituted imine III.


\[ \text{(CF}_3\text{)}_2\text{CF}_\text{N} \quad \text{CF}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3\text{C} \quad \text{CF}_3 \quad \text{CF}_3 \text{N} \left\langle \text{CF}(\text{CF}_3)_2 \right. \]

III

Analysis of the temperature dependence of the fluorine spectrum yielded an activation energy of $13 \pm 3$ kcal./mole. Replacement of the exchangeable imine proton with a methyl group in the ketimine systems
investigated in the present work might permit the observation of rotation about nonfluorinated carbon-nitrogen double bonds. Methylamine Schiff bases were therefore made from s-butyl phenyl ketone, n-propyl phenyl ketone, ethyl phenyl ketone, diisopropyl ketone, and p-chlorobenzophenone. In all cases but the first, the N-methyl resonances consisted of a single sharp peak, indicative of fast exchange, the coincidence of chemical shifts, or the presence of only a single isomer. This was particularly surprising for the metmylimine of p-chlorobenzophenone, since Curtin and Hauser\textsuperscript{16} reported that the N-methyl resonance consisted of two peaks. The N-methyl resonance of s-butylphenylketone methylimine (IV) was a doublet, the components of which were separated by 1 c.p.s. The invariance of the peak separation to a change of field from 14,100 to 23,500 gauss\textsuperscript{21} identifies the doublet as a coupling, rather than a chemical shift. This is presumably a five-bond coupling between the N-methyl protons and the methinyl proton of the s-butyl group.\textsuperscript{22} The absence of chemically shifted

\textsuperscript{21} The author is indebted to Dr. Lois Durham, Stanford University, Stanford, California for recording the 100-Mc. p.s. spectra.

\textsuperscript{22}
N-methyl resonances for all members of this series renders impossible the study of isomerization about the carbon-nitrogen double bond by n.m.r. methods. 23

Experimental

Melting points and boiling points are uncorrected. Melting points were measured on either the Büchi or the Hershberg apparatus. Proton magnetic resonance spectra were measured on the Varian Associates Model A-60 spectrometer operated at 60.0 Mc. p. s. and 14, 100 gauss. The authors would like to thank Drs. S. L. Manatt and D. D. Elleman of the Jet Propulsion Laboratory, Pasadena, California, for the use of a temperature-adaptable A-60.
Benzamide-\textsuperscript{15}N. – A 100-ml. three-necked round-bottomed flask was equipped with an inlet tube for dry nitrogen, a dropping funnel, and a reflux condenser leading through two potassium hydroxide drying tubes to a second flask. The latter 200-ml. round-bottomed flask was equipped with the inlet tube, a mechanical stirrer, and an exit tube which led through a trap to a 10% hydrochloric acid solution. After nitrogen flow was initiated, the second flask was flamed out several times and filled with 4.38 g. (0.0312 mole) of benzoyl chloride and 120 ml. of anhydrous ether. The stirred ether solution was cooled in a Dry Ice-acetone bath, and ammonia was introduced slowly. The ammonia was generated in the first flask by the dropwise addition of 3 g. (0.0550 mole) of concentrated aqueous ammonium-\textsuperscript{15}N chloride (Merck Sharpe and Dohme of Canada) to a refluxing solution of 5.7 g. of sodium hydroxide in 14 ml. of water. An hour and a half after evolution of ammonia had ceased, the second flask was warmed to room temperature and allowed to stand for 12 hrs. There was no ammonia trapped in the hydrochloric acid solution. The ether solution was filtered, and the solid was washed with five 18-ml. portions of absolute ethanol. The filtrate was concentrated to incipient crystallization by rotary evaporation, and 75 ml. of benzene was added. The solution was filtered at its boiling point, and the residue was washed with three 35-ml. portions of hot benzene. Two crops of benzamide, totaling 1.582 g., were obtained from this solution. The original solid by-product was washed with acetone. This solution eventually produced an additional 1.428 g. of the product. The total yield of benzamide-\textsuperscript{15}N was 3.010 g. (0.0246 mole, 89.5%), m.p. 122.8–123.2° (reported 121–123°).\textsuperscript{24} The excess ammonium chloride...

(1.58 g.) was recovered quantitatively.

**Benzonitrile-15N.** — Benzamide-15N (1.582 g., 0.0130 mole) and sodium aluminum chloride (2.50 g., 0.0130 mole) were mixed carefully in a 50-ml. round-bottomed flask equipped with a distillation head. The mixture was heated in a silicone oil bath at 180° until effervescence ceased. Heating was continued with a free flame until distillation of the product was finished. The yield of benzonitrile-15N was 0.995 g. (0.00956 mole, 73.5%).

**Diphenylketimine-15N.** — Phenyl Grignard reagent was prepared from 3.16 g. (0.0201 mole) of bromobenzene and 0.500 g. (0.0206 mole) of magnesium in 30 ml. of anhydrous ether contained in a 100-ml. three-necked round-bottomed flask equipped with a dropping funnel and a reflux condenser. Benzonitrile-15N (1.87 g., 0.0180 mole) in 10 ml. of anhydrous ether was added dropwise at room temperature, and the mixture was mechanically stirred for 7.5 hrs. The solution was cooled, and 3.61 g. of anhydrous methanol was added carefully at room temperature. The resulting gum was stirred for 30 min. until it became completely crystalline. The slurry was filtered, and the ether and excess methanol were removed by distillation. The residue on distillation gave 2.16 g. (0.0121 mole, 67.2%) of diphenylketimine-15N, b. p. 120° (1 mm.), \( n_D^{37} = 1.6088 \).
Diphenylketimine-$^{15}$N Hydrochloride. — A 200-ml. three-necked round-bottomed flask was flamed out and filled with 0.681 g. (0.00380 mole) of diphenylketimine-$^{15}$N and 80 ml. of diethyl ether which had just been distilled from lithium aluminum hydride. A nitrogen atmosphere was maintained in the flask throughout the reaction. Hydrogen chloride gas was bubbled through a sulfuric acid trap into the ether solution until no more precipitate formed. The solid was isolated by filtration and dried under vacuum in a desiccator. The yield of diphenylketimine-$^{15}$N hydrochloride was 0.643 g. (0.00298 mole, 78.4%).

$i$-Butylphenylketimine-$^{15}$N was prepared in the same manner as diphenylketimine-$^{15}$N (vide supra) from 4.50 g. (0.0328 mole) of $s$-butyl bromide, 0.77 g. (0.0140 mole) of magnesium, 1.60 g. (0.0154 mole) of benzonitrile-$^{15}$N, and 3.8 g. of anhydrous methanol. The yield of ketimine (1.689 g., 0.0104 mole) was 74.3%.

Potassium cyanide-$^{15}$N was obtained from Volk Radiochemical Laboratories.

$n$-Butyl Cyanide-$^{15}$N. — $n$-Butyl chloride was added dropwise over a period of 40 min. to a solution of 1.09 g. (0.0165 mole) of potassium cyanide-$^{15}$N and 1.0 g. of sodium acetate in dimethyl sulfoxide heated at 120° in a 100-ml. three-necked round-bottomed flask equipped with a thermometer, reflux condenser, and dropping funnel. After the solution had refluxed for 18 hrs., water was added,
and the nitrile was removed by extraction with three portions of diethyl ether. Hydrochloric acid was added to hydrolyze any isocyanate that might have been present, and the solution was again extracted with ether. The ether was removed by distillation, and the product was dried over calcium chloride and phosphorus pentoxide. The yield of n-butyl cyanide-$^{15}$N (valeronitrile-$^{15}$N) was 1.007 g. (0.0120 mole, 72.7%).


Di-n-butylketimine-$^{15}$N was prepared in the same manner as diphenylketimine-$^{15}$N (vide supra) from 3.0 g. (0.0219 mole) of n-butyl bromide, 0.50 g. (0.00910 mole) of magnesium, 1.007 g. (0.0120 mole) of n-butyl cyanide-$^{15}$N, and 3.2 g. of anhydrous methanol. The yield of ketimine (0.533 g., 0.00375 mole) was 41.2%.

$^\beta$-Butyl phenyl ketone. — A 1-1. three-necked round-bottomed flask equipped with a gas-inlet tube, a reflux condenser, and a dropping funnel was flamed out and flushed with argon. Benzonitrile (40 g., 0.388 mole) was added dropwise with stirring to a Grignard reagent formed from 68.5 g. (0.500 mole) of $^\beta$-butyl bromide and 12.4 g. (0.510 mole) of magnesium in 500 ml. of anhydrous ether. The yellow-gray mixture was refluxed for 12 hrs. After the mixture had cooled to room temperature, 96 g. of methanol was added very slowly with agitation. The precipitate was removed by filtration when it had become completely crystalline. Methanol (100 ml.) containing 10 ml. of water was added, and the solution was allowed to stand for
an hour. The ether and methanol were removed by distillation at atmospheric pressure, and the residue was fractionated at 5 mm. After benzonitrile was removed at 72−3°, two fractions (94−7°, 97−100°) of ketone−ketimine were collected. The mixtures were treated with water until VPC traces showed no ketimine to be present.

N-Methyl−s-butylphenylketimine. — The crude s-butyl phenyl ketone (5 g.) prepared as described above was placed in a 15-ml. heavy-walled ampoule and degassed three times at 0.1 mm. to remove all traces of ammonia. Methylamine (1 g.), prepared by the addition of potassium hydroxide solution to the stock 40% aqueous solution, was distilled under vacuum into the ampoule, which was sealed at atmospheric pressure and heated at 175° for 3 days. An aqueous layer separated. The tube was opened, the water was removed, and four additional milliliters of amine were distilled under vacuum into the tube, which was again sealed and heated at 175° for 1 day. No further reaction was evident, so the tube was opened and the contents distilled, b.p. 67° (1 mm.). VPC analysis showed the distillate to contain about 60% ketimine and 40% ketone. Pure samples of the former were obtained by preparative vapor phase chromatography.
Fig. 1. — Proton spectrum of diphenylketimine, –40°.
Fig. 2. -- Temperature dependence of the imine proton resonance in diphenylketimine-15N.
Fig. 3. — Proton spectrum of $\alpha$-butylphenylketimine–$^{15}$N, $-60^\circ$. 
Fig. 4. --- Temperature dependence of the imine proton resonance of S-butyrylphenyketimine$^{15}$N. The calculated curves were derived from $P_A(-60^\circ) = 0.39, P_B(-60^\circ) = 0.61, T_2 = 1.89$ sec. and $\delta$ (slow exchange) = 11.0 c. p. s. The populations were corrected for changes with temperature ($\Delta F = 70$ cal.). The $\tau_A$ values which correspond to the calculated curves are (top to bottom): 0.040, 0.055, 0.075, 0.095, 0.130, and 0.250 sec., respectively. The bottom curve corresponds to the slow-exchange limit ($\tau_A \geq 1.0$).
Fig. 5. — Arrhenius plot for diphenylketimine$^{15}$N.
Fig. 6. — Arrhenius plot for $\alpha$-butylphenylketimine$^{-15}$N.
The imine protons of nitrogen-15 labeled ketimines exhibit temperature-dependent nuclear magnetic resonances. Analysis of the effect of concentration of substrate on the mean lifetime indicates that the spectral changes result from a bimolecular exchange of protons between imines. The activation energy of this process in diphenylketimine-$^{15}$N was determined to be $13.8 \pm 2$ kcal/mole, whereas in $s$-butylphenylketimine-$^{15}$N, the activation energy was about 6 kcal/mole. In the latter case, separate resonances were observed for the distinct syn and anti isomers.
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