

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HAVERFORD COLLEGE, HAVERFORD, PA.]

Kinetics of the Thermal Interconversion of 2-Methylmethylenecyclopropane and Ethylidenecyclopropane¹

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The kinetics of the reversible thermal interconversion of the two isomeric methylmethylenecyclopropanes, 2-methylmethylenecyclopropane and ethylidenecyclopropane, have been studied in the gas phase between 197.2 and 233.8° at reactant pressures of about 25 cm. The equilibrium constant $K = 1.30$ at 210° for the 2-methylmethylenecyclopropane-ethylidenecyclopropane reaction; $\Delta H^\circ = -0.57 \pm 0.20$ kcal./mole, using equilibrium constant determinations up to 300°. Kinetics for a reversible first-order system were found; rate constants were insensitive to a variation of a factor of six in reactant pressure, and the rate increased by less than 6% in runs using reaction vessels packed with glass wool. Thus the reaction observed is probably a homogeneous unimolecular reaction. $(k_1 + k_2) = 10^{14.26} \exp(-40.4 \pm 0.6) \text{ kcal./RT} \text{ sec.}^{-1}$ for the reversible first-order system, where $K = k_1/k_2$. Using recently determined values for the heats of hydrogenation of these species, it is concluded that the low energy barrier of 40 kcal./mole found for this reaction, relative to the value of 47–57 kcal./mole taken as the energy barrier to the opening of the ring of methylenecyclopropane without any assistance from allylic resonance, indicates that recently published arguments for "steric inhibition of resonance" in the methylenecyclobutane decomposition cannot be extended to this system.

Introduction

In a screening of possible reactions of simple hydrocarbon molecules to obtain data on low pressure phenomena connected with unimolecular reactions, methylenecyclopropane was considered. Preliminary experiments² indicated that this molecule was approximately as stable as methylcyclopropane.³ At 445° and 2 mm. pressure the half-life for decomposition to assorted products was about 10⁴ sec. However, the complexity of the system, including polymerization at higher pressures, temporarily cooled interest in studies of thermal reactions of this molecule. One reaction which was considered but which could not be followed without some variety of labeling was the "chemical pseudo-rotation" which would take place on rupture of the 2–3 bond of the ring and subsequent closure with the previously exomethylene carbon. A concerted process or assistance through formation of an intermediate allylic system as well as additional ring strain might reduce the barrier for this process from the value of ca. 65 kcal./mole observed for opening the cyclopropane ring system down to some considerably lower figure. This would give the chemical pseudo-rotation at a temperature much lower than that required to destroy the ring system.

Frey⁴ has reported the formation of excited methylenecyclopropane from the reaction of photochemically produced methylene with allene. This highly excited methylenecyclopropane was then found to decompose to acetylene and ethylene as well as isomeric C₄H₆ compounds if not stabilized by collisions. Doering and Leermakers⁵ have observed incorporation of deuterium into the exomethylene group on reaction of allene with CD₂ in the gas phase, indicating that the chemical rotation was occurring in the excited methylenecyclopropane molecule.

In a recent communication, Nangia and Benson⁶ have examined the energy barriers for the decomposition of methylenecyclobutane⁷ (63.3 kcal./mole), methylcyclobutane⁸ (62.5 kcal./mole), vinylcyclopropane⁹ (49.6 kcal./mole), and cyclopropane¹⁰ (65 kcal./mole). The view is taken that the decompositions proceed

through a distinct diradical intermediate. The over-all activation energy for decomposition to stable products is explained to be approximately that of the ring-rupture step. Vinylcyclopropane is thought to have a lower barrier for ring opening than does cyclopropane because the vinyl group can be oriented so that an allylic system is formed on opening of either of two of the three cyclopropane ring bonds. Rupture of a 2–3 carbon-carbon bond in methylenecyclobutane does not lead to an allylic system without rotation of the proper CH₂ group, and hence the similar barriers for the methylene and methylcyclobutane decompositions are taken by Nangia and Benson to be evidence for the steric inhibition of resonance in this system. Extension of the arguments of Nangia and Benson to methylenecyclopropane would indicate that there should also be steric inhibition to assistance from allylic radical formation on opening the ring. The barrier to the chemical pseudo-rotation should be comparable to that for the reactions of alkylcyclopropanes with allowances to be made for effects of any increased ring strain introduced by the exomethylene group. Thus a determination of the activation energy for the chemical pseudo-rotation of the methylenecyclopropane system might provide a test of the generality of the arguments of Nangia and Benson.

The introduction of a methyl group should not greatly change the energetics of the methycyclopropane system, and such a substitution permits observation of the reaction in question by examination of chemically different products; hence the following work was undertaken with the methyl derivative.

Experimental

Preparation of Ethylidenecyclopropane and 2-Methylmethylenecyclopropane.—The preparation of a mixture of ethylidenecyclopropane and 2-methylmethylenecyclopropane was effected by the catalytic addition of methylene from diazomethane to methylallene. Twelve grams of methylallene (Columbia Organic Chemicals) was distilled into a cold reaction vessel with 10 ml. of *n*-hexane as a solvent, and the cuprous chloride-catalyzed reaction of the diazomethane generated from 17 g. of *N*-nitroso-*N*-methylurea was carried out as described previously.¹¹ Analysis of the product mixture using a 12-ft. GE SF-96 silicone oil on firebrick g.l.p.c. column at room temperature showed methylallene, two major product peaks, and *n*-hexane emerging with retention times of 14, 28, 46, and 78 min., respectively. The ratio of the more to less volatile of the two product peaks was 1.2/1.0. The total reactant conversion was about 15%.

After a preliminary removal of the bulk of the methylallene by fractional distillation using a Todd column, the products were separated by g.l.p.c. using a 0.5 in. diameter by 5 ft. long preparative column packed with SF-96 silicone oil on firebrick. Samples of the two products were taken for mass, n.m.r., and infrared

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 3, 1963.

(2) J. P. Chesick, unpublished work.

(3) J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960).

(4) H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961).

(5) W. v. E. Doering, private communication.

(6) P. Nangia and S. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962).

(7) J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

(8) M. Das and W. Walters, *Z. physik. Chem.* (Frankfurt), **15**, 22 (1958).

(9) M. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

(10) T. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 399 (1934).

(11) J. P. Chesick, *ibid.*, **84**, 3250 (1962).

spectra. The mass spectra of both compounds (taken with the CEC 21-130 instrument of the Department of Chemistry, University of Pennsylvania) gave parent peaks at $m/e = 68$ with 67 as the principal peak. Other main peaks were at 53, 41, 40, 39, and 27. The chief difference in the two spectra was that the 68/67 ratio for the lower boiling isomer was 0.42, while this ratio was 0.68 for the higher boiling isomer. N.m.r. spectra (Varian A-60 spectrometer, Princeton University, courtesy of Professor Paul Schleyer) were taken of samples of the two products as well as a sample of methylene cyclopropane prepared by the procedure of Gragson, *et al.*¹² The methylenecyclopropane spectrum showed a symmetrical quintet at $\tau = 4.75$ and a triplet at $\tau = 9.00$ with an area ratio of 1.0/2.0. The spectrum of the lower boiling product showed a multiplet at $\tau = 4.75$, a multiplet at $\tau = 8.75$ superimposed on a sharp doublet at $\tau = 8.88$, and a third multiplet at $\tau = 9.36$. A single integral trace gave the areas as approximately 2/5.5/0.9 for the three multiplets. The spectrum of the higher boiling product, which was taken in a more concentrated solution and gave more precise integrals than the other sample, showed a symmetrical multiplet at $\tau = 4.37$, a doublet at $\tau = 8.23$, and a third group of lines at $\tau = 9.03$. The relative integrals were 1.00/3.03/4.05. The infrared spectrum of the lower boiling isomer was quite similar to that of methylenecyclopropane between 2000 and 800 cm^{-1} with double bond stretching and deformation bands at 1750 and 890 cm^{-1} . The higher boiling isomer also showed an absorption at 1800 cm^{-1} and the 890 cm^{-1} band of the other isomer was shifted down to 780 cm^{-1} . It is concluded that the early eluting, more volatile isomer is 2-methylmethylenecyclopropane, and that the higher boiling substance is ethylidenecyclopropane.

A sample of the methylmethylenecyclopropane was hydrogenated over platinum black in glacial acetic acid, and the products were found to be *cis*-1,2-dimethylcyclopropane, *n*-pentane, and isopentane as determined by mass and infrared spectra and g.l.p.c. retention times. Ethylidenecyclopropane gave ethylcyclopropane and the two pentanes on reduction. The amounts of hydrogenolysis appeared to increase with time after a rapid initial hydrogen uptake.

Kinetic Measurements.—Reactions were carried out in sealed Pyrex ampoules of 6-mm. diameter standard wall Pyrex tubing, 5 cm. long. These ampoules were well evacuated and flamed before filling. A pressure of 2 to 3 mm. of either of the reactant species in the vacuum line was condensed in the ampoule by liquid nitrogen, and the ampoule was sealed. The ampoule to vacuum line volume ratio was calculated to give a pressure of approximately 25 cm. in the ampoule when the sample was vaporized. Thus it is certain that no liquid remained in the ampoules at even 100°, well below the temperature of the reaction. Some ampoules were packed with Pyrex glass wool before filling to test for surface effects. This packing increased the surface to volume ratio by a factor of 30. Kinetic runs were made by immersing the ampoules in a well stirred and thermostated wax bath and then quickly quenching the ampoules on removal from the bath after the desired time interval. The times for heating and quenching of the small ampoules were small compared to the reaction times. The bath temperature was regulated to $\pm 0.07^\circ$ except at the highest two temperatures employed where use of another regulator element permitted control only to $\pm 0.16^\circ$. The bath temperature was homogeneous to better than $\pm 0.02^\circ$ in the region of the sample tubes. Temperatures were measured and monitored by means of a calibrated four-junction chromel-P alumel thermocouple and Leeds and Northrup type K-3 potentiometer. A tube furnace was used to equilibrate samples at temperatures up to 300° to permit determination of the equilibrium constant over a wider temperature range than allowed by the kinetic runs in the wax bath. The ampoules containing the product mixtures were broken *in vacuo* and the total contents were vaporized from the gas injection trap of an Aerograph A90-P chromatograph into a 12 ft. SF-96 silicone on firebrick column at 60°. Peak areas used for measurements were taken from the recorder integrator tracings.

Results

At temperatures high enough so that equilibrium could be attained in a reasonable period of time, either ethylidenecyclopropane or 2-methylmethylenecyclopropane gave the same equilibrium mixture of the starting material and one product. The product in both cases had the same g.l.p.c. retention time and infrared spectrum as the other isomer produced in the synthesis.

Kinetic runs were made at seven temperatures in the range 197.2 to 233.8° with an average of over five

(12) J. Gragson, K. Greenlee, J. Derfer, and C. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

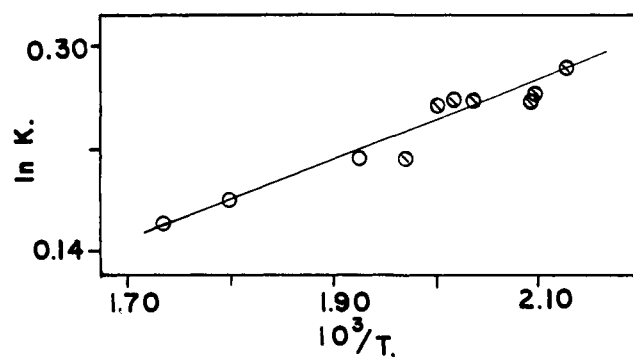
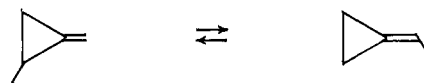


Fig. 1.—Temperature dependence of the methylmethylenecyclopropane-ethylidenecyclopropane equilibrium constant: \odot , data from kinetic runs; \circ , data from higher temperature equilibrium mixtures.

runs at each temperature. The reaction was followed over a range of values of the quantity $X_{00}/(X_{00} - X)$ up to at least 2, and usually higher, at each temperature. Here X is the mole fraction of the product species at a given time and X_{00} is the equilibrium value. Ampoules containing samples of each isomer were usually heated together for equal times, and the reaction was observed to follow reversible first-order kinetics. Samples were heated in the tube furnace at temperatures up to 300° to obtain better data for the temperature dependence of the equilibrium constant than was possible in the more restricted temperature region of the kinetics work. Two runs in tubes packed with glass wool yielded an average rate constant 5% higher than found in two samples in unpacked tubes at the same temperature. Since a chain reaction with chains both initiated and broken at the surface is unlikely at these temperatures in this type of reaction, the lack of any gross changes in reaction rate in the packed tube runs seems to indicate that the homogeneous reaction has been observed.

Although most tubes were filled with a quantity of material which should result in a final pressure of about 25 cm., three tubes were filled with a sixth of the usual reactant pressure, giving no appreciable change in rate constants. It is not likely, considering pressure dependencies of rate constants in other unimolecular isomerizations of hydrocarbon molecules of similar complexity such as methylcyclopropane³ or bicyclopentane,¹³ that any low pressure drop-off in unimolecular rate constants would be observable in this work, and high pressure values are being obtained.

The equilibrium constant for the reaction



ranged between the limits of 1.18 at 300° and 1.33 at 197°. A plot of $\ln K$ vs. $1/T$, Fig. 1, gives $\Delta H = -0.5 \pm 0.2$ kcal./mole, and therefore $\Delta S = -0.55$ e.u. for this interconversion reaction, or $\exp(\Delta S/R) = 0.75$.

An Arrhenius plot, Fig. 2, of the sum of the two first-order rate constants ($k_1 + k_2$) obtained from the kinetic data, where $K = k_1/k_2$, gives

$$(k_1 + k_2) = 10^{14.26} \exp\{(-40.4 \pm 0.6) \text{ kcal./RT}\} \text{ sec.}^{-1}$$

Discussion

The small value of the observed ΔH for the isomerization indicates that the two positions for the methyl group are energetically similar and that methyl sub-

(13) M. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

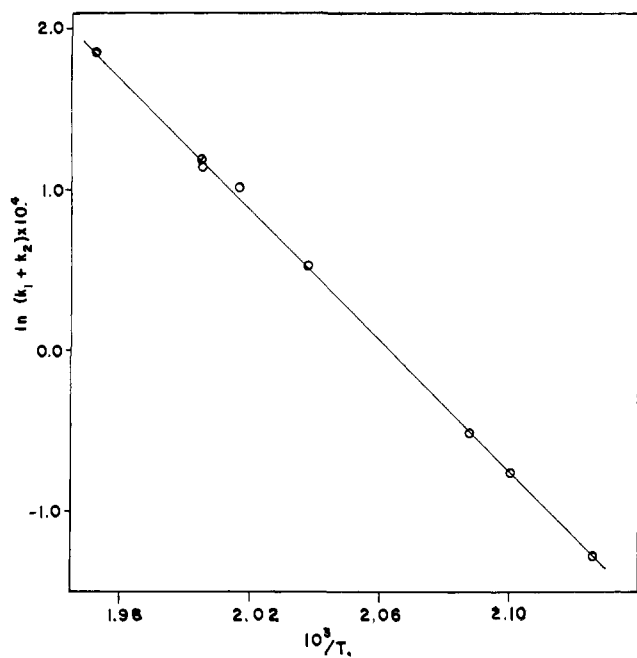


Fig. 2.—Arrhenius plot of rate constant sum: \odot , packed ampoule runs.

stitution has probably had little effect on the energetics of the reaction.

No values were hitherto available for either the heat of combustion or of hydrogenation of the methylenecyclopropane ring system. The heats of hydrogenation of pairs of samples of methylmethylenecyclopropane and ethylenecyclopropane to the alkylcyclopropanes in glacial acetic acid were determined by Turner and found to be 38.0 ± 1.0 kcal./mole and 35.5 ± 1.0 kcal./mole, respectively.¹⁴ The uncertainties are due chiefly to the hydrogenolysis of ca. 25% of the alkylcyclopropanes to *n*- and isopentanes. These numbers may be compared to the value of 29.4 kcal./mole found for the heat of hydrogenation of methylenecyclobutane using the same solvent system.¹⁵

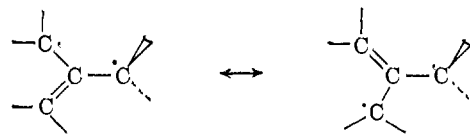
Thus there appears to be an additional strain energy in the methylenecyclopropane ring system of $36.8 - 29.4 = 7.4$ kcal./mole relative to the reference compound methylenecyclobutane. It will be recalled that methylenecyclobutane showed essentially the same barrier for decomposition as methylcyclobutane.

Two approaches are then possible for estimating limits to the barrier for isomerization assuming steric inhibition of resonance in the transition state. If 82 kcal./mole is taken as the value for a "normal" sp^3-sp^3 carbon-carbon bond, then the value of 27.6 kcal./mole for the excess energy of cyclopropane obtained from the heats of combustion of cyclic alkanes, measured by Kaarsemaker and Coops,¹⁶ gives 54.4 kcal./mole for the ΔH of forming a hypothetical trimethylene diradical in its lowest energy rotational conformation and with no bonding between the terminal carbons, starting from cyclopropane. Benson¹⁷ derives a similar number from other bond energy data which he used to calculate the heat of formation of the trimethylene diradical. Subtraction of the 7.4 kcal. of extra strain found from the heats of hydrogenation gives 47 kcal./mole as the minimum ΔH for forming the species $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$ from methylenecyclopropane assuming

steric inhibition of resonance. This 47 kcal./mole is significantly above the observed barrier for the methyl isomer interconversion reaction.

Another approach which may take a more realistic account of activation energy barriers is to use the observed value of 64 kcal./mole for the barrier to the *cis-trans* isomerization of 1,2-dideuteriocyclopropane.¹⁸ This number is larger than the ΔH for cyclopropane ring opening, an effect which has been attributed to internal rotational energy barriers and/or bonding decreasing more rapidly than ring strain with increasing C-C-C bond angle. Subtraction of 7.4 kcal. for the additional strain in the methylenecyclopropane system then gives 56.6 kcal. for the predicted isomerization barrier. It is therefore concluded from the lower value of 40.6 kcal. observed experimentally for the barrier that the transition state in the reaction is loose enough to permit some assistance through allylic resonance. This is in contrast to the conclusions previously recorded for the cyclobutane system.⁶ A concerted bond forming-bond rupture process is also possible for the methylenecyclopropane system which may make the concept of a distinct diradical intermediate unduly simplified. The possibility for a concerted reaction also exists for the vinylcyclopropane isomerization without the existence of the diradical entity $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$.

In conclusion, there are factors involved in predictions of activation energies for these small ring isomerizations and decompositions which should be emphasized. The extent of ring opening in the transition state will determine the amount of ring strain relieved. The structure of the transition state is not well defined and will strongly influence the energetics of the reaction if π -electron systems are involved. For example, simple Hückel molecular orbital arguments give a delocalization energy of zero, relative to ethylene, for the species formed on rupture of the methylenecyclopropane ring without allowing rotation of any CH_2 groups. This corresponds to complete steric inhibition of resonance in the transition state. The chemical pseudo-rotation reaction reported here involves the eventual rotation of two CH_2 (or CH_2 and $CH(CH_3)$) groups by 90° . A stepwise process involving rotation of one group leaving two CH_2 groups in the plane of the carbon atoms and one group out of the plane gives an allylic system with a delocalization



energy of 0.8β . This energy is suggested from bond energy considerations to be 20 kcal./mole.¹⁹ A completely planar trimethylenemethane resulting from rotation of two groups has a delocalization energy of 1.5β , relative to ethylene. If π -electron energies govern, the symmetric-planar trimethylenemethane is then considerably lower in energy than any non-planar opened ring species and therefore may be an intermediate, although not necessarily the transition state which determines the activation energy for the reaction. The actual transition state for the reaction may well be one resulting from a concerted process in which two CHR groups are in planes approximately 45° from the plane of the carbon atoms and the third group is perpendicular to the carbon plane. The energy barrier for the formation of this species is then

(14) R. Turner, Rice University, private communication.

(15) R. Turner, Kekulé Symposium Papers, Butterworths Sci. Publ., London (1959).

(16) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

(17) S. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(18) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

(19) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 393.

not predictable with any accuracy by a simple model or comparison.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. XII. Aniline

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Several of the ionization-dissociation processes of aniline under electron impact have been deduced from the mass spectra of anilines unlabeled and labeled in three ways: *-3-d*, *-2,4,6-d₃*, and *-N¹⁵*. The major primary process involves loss of HCN; minor competing processes involve loss of H, CH₃, NH₂, C₂H₂, and C₂H₃. The nitrogen atom clearly plays a central role in determining the course of reaction of the aniline ion.

Although aniline bears a structural resemblance to toluene, the mass spectra of the two compounds³ differ markedly. The parent ion is by far the most abundant ion in the spectrum of aniline. The most abundant ion in that of toluene is formed by loss of a hydrogen atom; the corresponding product in the aniline spectrum is a distinctly minor one. The most abundant fragment ion from aniline is that of mass 66, formed apparently by loss of HCN from the parent ion; analogous loss of C₂H₂ from toluene is barely perceptible. The sharp differences found between the gross behavior of aniline and toluene prompted a closer examination of the former.

Spectra of labeled species of other compounds have helped clarify many ionization-dissociation processes induced by electron impact.⁴ An earlier study of the aniline spectrum⁵ was handicapped by the mass equivalence of a nitrogen atom and a methylene group; much of this difficulty can be removed by labeling with N¹⁵. We have therefore studied the mass spectra of aniline unlabeled, *-3-d*, *-2,4,6-d₃*, and *-N¹⁵*. The general procedure followed in interpreting the spectra of labeled compounds has been described elsewhere.⁴

Experimental

Aniline-*-3-d* and *-N¹⁵* were available from an earlier study.⁶ We are indebted to John G. Burr, Jr., of North American Aviation, for the gift of a sample of aniline-*-2,4,6-d₃*.⁷ Unlabeled aniline was redistilled commercial material. Isotopic composition of the labeled species was determined by mass spectrometry at reduced ionizing voltage⁸: aniline-*-3-d*, 95.8%; aniline-*-2,4,6-d₃*, 96.8% (*-d₀*, 0.2%; *-d₂*, 2.5%; *-d₄*, 0.5%); and aniline-*-N¹⁵*, 31.9%.

Spectra were measured with 70 e.v. on a Consolidated model 21-103c instrument. Partial spectra, shown in Table I, have been corrected for unlabeled aniline in the labeled materials and for naturally occurring heavy isotopes. For peaks in the parent-mass region, the latter correction was based on the known natural abundance of C¹³ and N¹⁵. For all other peaks, the possible presence of nitrogen was disregarded, and an approximate correction was made using factors derived for hydrocarbon ions of the same masses.⁹ The complete spectra will be submitted for publication elsewhere.³

The spectrum obtained for unlabeled aniline is closely similar to a previously published one⁵ except that it contains a normal peak at mass 78 and metastable peaks at 91.1, 64.1, and 46.8, none of which was reported in the earlier work.

(1) Engelhard Industries, Newark, N. J.

(2) Summer research participant from Department of Chemistry, University of Notre Dame.

(3) American Petroleum Institute, Research Project 44, "Catalog of Mass Spectral Data," Chemical Thermodynamics Properties Center, Agricultural and Mechanical College of Texas, College Station, Tex., 1947-1963.

(4) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.

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(6) T. J. Prosser and E. L. Eliel, *J. Am. Chem. Soc.*, **79**, 2544 (1957).

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(8) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

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Decomposition Reactions

At least seven decomposition reactions can be deduced from the spectra

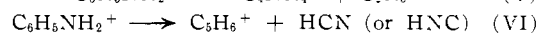
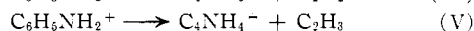
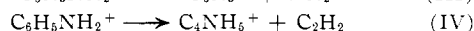
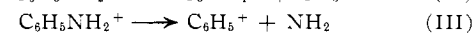
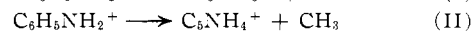


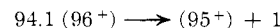
TABLE I

<i>m/e</i>	PARTIAL MASS SPECTRA OF ANILINES			
	Unlabeled	<i>-3-d</i>	<i>-2,4,6-d₃</i> ^a	<i>-N¹⁵</i>
65	18.4	4.66	3.57	17.0
66	32.4	17.6	3.41	32.8
67	3.21	31.6	6.23	2.5
68	..	2.07	17.4	3.0
69	28.7	0.1
70	0.61	..
76	1.22	0.61	.64	1.2
77	1.17	0.96	.43	1.4
78	1.94	1.95	.71	0.0
79	..	1.06	1.13	2.0
80	2.03	..
81	0.19	..
91	1.05	0.35	.12	0.0
92	10.8	1.13	.17	0.9
93	100.0	10.2	.0	11.7
94	..	100.0	1.85	100.0
95	11.8	..
96	100.0	..
97	0.3	..

^a Uncorrected for 2.5% *-d₂* and 0.5% *-d₄*.

Independent supporting evidence for reactions I, VI, and VII is provided by metastable peaks.^{4,10}

I. C₆H₅NH₂⁺ → C₆NH₆⁺ + H.—This reaction is the source of the normal peaks of parent mass less one and of the metastable peaks



in the spectra of aniline unlabeled, *-3-d*, and *-2,4,6-d₃*, respectively. The source of the hydrogen atom is not completely defined, because even small uncertainties in the isotopic analyses would result in proportionately large errors at the parent mass less one. Nonetheless, most of the hydrogen lost is evidently protium in all the spectra and therefore comes from the amino group. Similarly, the C₆NH₅⁺ ion evidently arises by loss of H₂ or 2H chiefly from the amino group.

(10) H. M. Rosenstock, A. L. Wahrhaftig, and H. Eyring, "The Mass Spectra of Large Molecules. II. The Application of Absolute Rate Theory," University of Utah, Salt Lake City, Utah, 1952, p. 95 ff.