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The Activation Energy of Inversion in Substituted 1-Methylaziridines (N-Methylethylenimines) Measured by the Nuclear Magnetic Resonance Technique[1]

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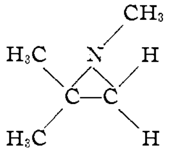
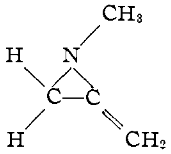
The activation energy, ΔE, and frequency factor, ν_0, for inversion in 1-methyl-2,2-dimethylaziridine (I) and 1-methyl-2-methyleneaziridine (II) have been measured using the n.m.r. technique. The results are $\Delta E = 10.0$ kcal. and $\nu_0 = 5 \times 10^7$ sec.$^{-1}$ for I and $\Delta E = 6.4$ kcal. and $\nu_0 = 1 \times 10^9$ sec.$^{-1}$ for II. ΔE and ν_0 have also been measured for solutions of I in methanol and carbon tetrachloride. The results are: $\Delta E = 6.8$ kcal., $\nu_0 = 2 \times 10^5$ sec.$^{-1}$ and $\Delta E = 7.8$ kcal., $\nu_0 = 1 \times 10^6$ sec.$^{-1}$, respectively.

Rapid inversion of the geometrical configuration of the groups bonded to nitrogen in ammonia and related molecules has been known for a long time. The main evidence for this phenomenon has come from spectroscopic data (inversion spectra)[3] and the unsuccessful attempts to resolve trivalent nitrogen compounds into optical isomers.[4] Several calculations have been made of the energy barriers of the inversion process[4]; however, all lack experimental support. It has been pointed out by several investigators that substituted aziridines (ethylenimines) might prove especially suitable for resolution into optically active antipodes because the strain in the three-membered ring should increase the activation energy for inversion in these compounds to perhaps as high as 20–40 kcal./mole.

Recently, the rates of inversion for several N-substituted aziridines have been measured by Bottini and Roberts,[4] using the n.m.r. technique. Heeschen and Gutowsky,[5] using the same method, have evaluated the activation energy of inversion for 1-methylaziridine and obtained $\Delta E = 19 \pm 3$ kcal./mole and a frequency factor of about 10^{11}. In this paper, measurements of the inversion rate as a function of the temperature for 1-methyl-2,2-dimethylaziridine (I) and for 1-methyl-2-methyleneaziridine (II), are reported.


I


II

The n.m.r. spectrum of I at room temperature is shown in Fig. 1. The resonance lines are attributed to the following groups: (A) the N-methyl, (B) the C-methyls and (C) the ring methylene. The spectrum indicates that the inversion rate of I is slow compared to the reciprocal of the chemical shifts between the protons of the two C-methyl groups or the ring methylenes. It should be noted that the C-methyl and ring methylene lines are further split because of spin–spin interactions involving neighboring groups. These splittings are small, however, compared to the chemical shifts and are not resolved in Fig. 1. When I is heated both doublets shown in Fig. 1 broaden and eventually collapse to two single lines of relative intensity 1:3 with a small chemical shift between them.

The n.m.r. spectrum of II, at room temperature, is shown in Fig. 2. The lines are attributed to the resonances of the following groups: (A) terminal methylene group, (B) N-methyl and (C) ring methylene. The terminal methylene and ring methylene lines are further split by spin–spin interactions (not resolved in Fig. 2). On cooling, the following changes in the spectrum are observed: (1) the terminal methylene resonance broadens and collapses to form a new, closely spaced multiplet (this occurs at about −25°) and (2) the ring methylene resonance broadens and eventually, on further cooling to about −70°, splits to form a fairly sharp doublet, with a frequency separation of about 50 c./s. The resolution at this low temperature was not good enough to permit observation of the presumed multiplet structure of the doublet components. One of the components of the doublet is very close to the N-methyl resonance. The N-methyl resonance itself does not show any significant change.

The rate of inversion for I has been evaluated through measurements of the changes in line shape of the doublet due to the non-equivalent C-methyls, as a function of temperature. The procedure was identical with that used previously for measuring the kinetics of hydrogen exchange in trimethylammonium ion.[6] Since the components of the doublet are quite broad, even when the inversion rate is slow, a large "natural" line width had to be used in the interpretation of the results. Similar corrections were applied previously in measurements of hydrogen exchange in N-methylacetamide.[7] The natural logarithm of the specific rate: $R \equiv 1/\tau$ (where τ is the mean life time of the molecule in a given configuration) as a function of the reciprocal of the absolute temperature is shown in Fig. 3. The activation energy obtained from the slope of the line in Fig. 3 is 10.0 ± 1.0 kcal./mole and the frequency factor ν_0 is 5×10^7 sec.$^{-1}$. Similar measurements have been carried out on

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[1] Supported by the Office of Naval Research.

[2] On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

[3] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 221. Also, W. Gordy, W. Y. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 127.

[4] References are given by A. T. Bottini and J. D. Roberts, THIS JOURNAL, **78**, 5126 (1956); **80**, 5203 (1958).

[5] (a) J. P. Heeschen, Ph.D. Thesis, University of Illinois, 1959; (b) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958).

[6] A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

[7] See Appendix A of the paper by A. Berger, A. Loewenstein and S. Meiboom, THIS JOURNAL, **81**, 62 (1959).

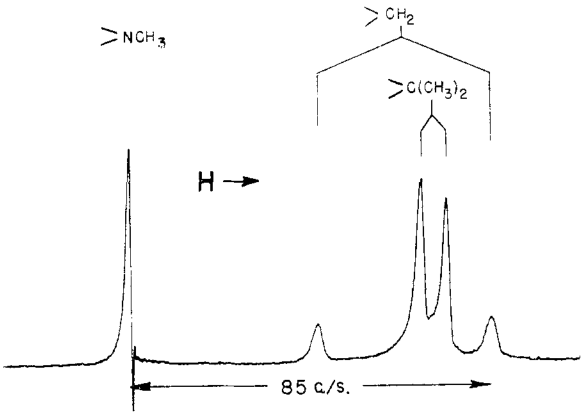

Fig. 1.—N.m.r. spectrum of 1-methyl-2,2-dimethylaziridine (I) at room temperature.

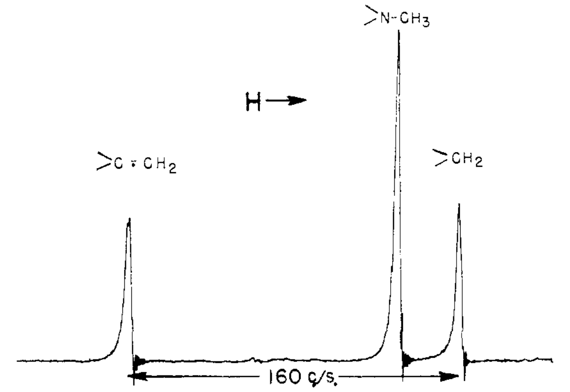

Fig. 2.—N.m.r. spectrum of 1-methyl-2-methyleneaziridine (II) at room temperature.

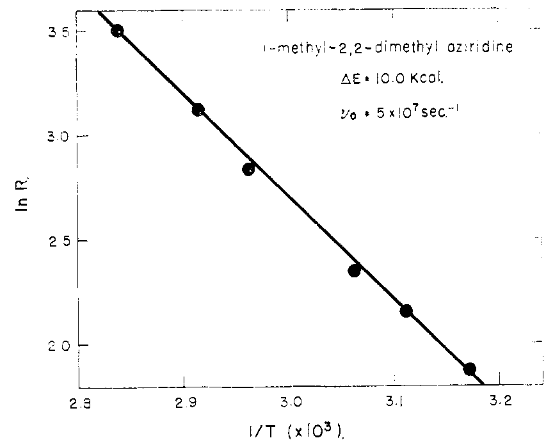

Fig. 3.—Plot of ln R as function of $1/T$ for compound I. T is the absolute temperature and $R \equiv 1/\tau$ where τ is the mean life time of the molecule in a given configuration.

solutions of I in methanol (slightly basic) and in carbon tetrachloride. The results are presented in Figs. 4 and 5. The activation energies and frequency factors are $\Delta E = 6.8 \pm 0.7$ kcal. and $\nu_0 = 2 \times 10^5$ sec.$^{-1}$ for the methanolic solution and $\Delta E = 7.8 \pm 0.8$ kcal. and $\nu_0 = 1 \times 10^6$ sec.$^{-1}$ for the carbon tetrachloride solution.

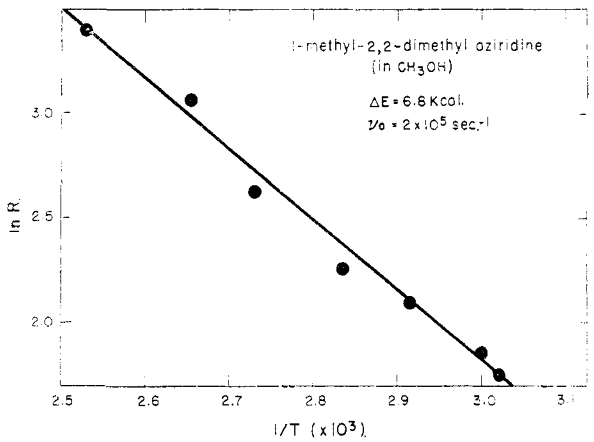

Fig. 4.—Plot of ln R as function of $1/T$ for a solution of I in basic methanol.

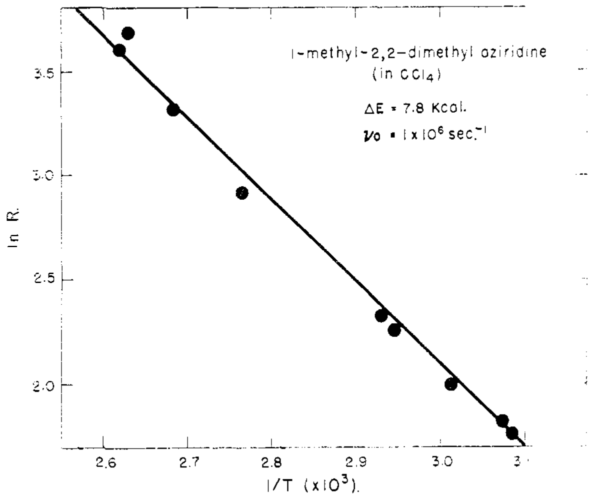

Fig. 5.—Plot of ln R as function of $1/T$ for a solution of I in carbon tetrachloride.

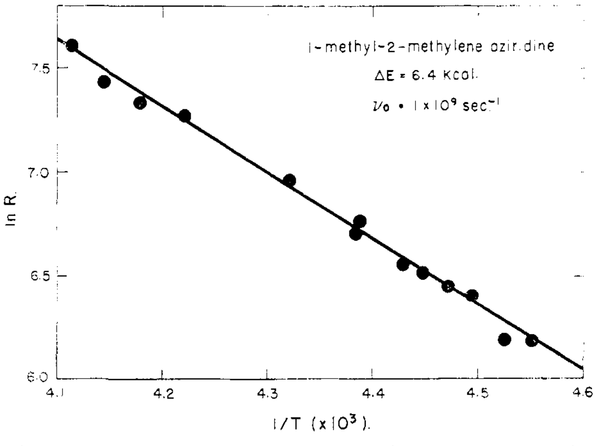

Fig. 6.—Plot of ln R as function of $1/T$ for compound II.

In the evaluation of the activation energy of II, the initial broadening of the ring methylene line was measured as the substance was cooled. The rate was calculated using the approximate equation applying for fast exchange as for measurements of exchange in aqueous hydrogen peroxide solutions.[8] The "natural" line width was estimated from the

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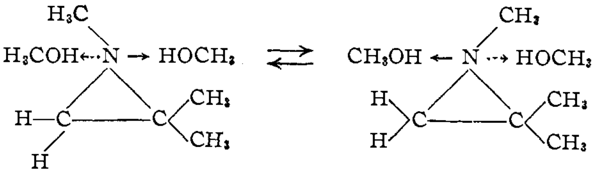
(8) M. Anbar, A. Loewenstein and S. Meiboom, THIS JOURNAL, **80**, 2630 (1958).

"width" of the ring methylene line at very fast exchange. The results are shown in Fig. 6. The activation energy obtained is $\Delta E = 6.4 \pm 0.6$ kcal. and $\nu_0 = 1 \times 10^9$ sec.$^{-1}$.

The measured activation energies for the two substituted 1-methylaziridines here investigated are very much smaller than most of the previous estimates and the experimental value obtained by Heeschen for 1-methylaziridine itself.[9] It is interesting that our activation energies are quite close to the calculated value of 6 kcal. given by Manning[10] for ammonia. The frequency factors, however, are much below the "normal" value of 10^{13}, indicating that the transmission coefficients are much smaller than unity. This, however, is not too surprising in view of the similar order of magnitude for ν_0 obtained for another "unimolecular" reaction of this type, namely, the rotation around the C–N bond in amides.[11,12]

The effect of solvents on the inversion of I is shown in Figs. 4 and 5. Both polar (methanol) and non-polar (carbon tetrachloride) solvents reduced the activation energy and frequency factor. It should be noted that the rate of inversion of I is considerably slower in methanolic solution than in the pure liquid or carbon tetrachloride. This has been attributed to the effect of hydrogen bonding between the hydroxyl group in methanol and the nitrogen atom in the aziridine ring.[4] However, it seems quite significant that the effect on such hydrogen bonding shows up in a greatly decreased frequency factor rather than in an increase in activation energy. This may be due to a bimolecular mechanism for inversion in methanol solution where one methanol molecule attacks the rear of the nitrogen in an imine–methanol, hydrogen-bonded complex.



It is clear that further experimental and theoretical investigation of these processes would be very fruitful.

Experimental

1-Methyl-2,2-dimethylaziridine (b.p. 67.8–68.2°) was prepared by alkaline treatment of the sulfonate ester salt of 2-N-methylamino-2-methyl-1-propanol. 1-Methyl-2-methyleneaziridine (b.p. 52.2–52.6°) was kindly supplied by Dr. A. T. Bottini.

All measurements were taken with the Varian model 4300B spectrometer. Frequency calibration was accomplished by the side-band technique. All measurements were performed at a proton frequency of 60 Mc., except those presented in Fig. 4, which were taken at 40 Mc. The measurements on pure I were taken at both 40 and 60 Mc.; the results were identical within the experimental accuracy.

Two types of inserts for heating and cooling were used: (1) the type described by Shoolery and Roberts[13] (supplied commercially by the Varian Associates) and (2) a modified type described by Fraenkel and Franconi.[12] The concentration of the solution of I in methanol and carbon tetrachloride was about 25% by volume. The methanol was made slightly basic by dissolving a small quantity of sodium in it. The purpose of the base was to inhibit reaction between the imine and methanol.[4]

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(9) The reason for the sizable differences between the measured values ΔE for our compounds and 1-methylaziridine[5] is not clear to us. It seems unlikely that the rather small change in structure could account for all of the discrepancy, which appears to be well outside experimental error.

(10) M. F. Manning, *J. Chem. Phys.*, **3**, 136 (1935).

(11) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(12) G. Fraenkel and C. Franconi, to be published.

(13) J. N. Shoolery and J. D. Roberts, *Rev. Sci. Instr.*, **28**, 61 (1957).

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[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part V. The Addition to Allyl and Methallyl Chlorides

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The addition of trichlorosilane, methyldichlorosilane, dimethylchlorosilane and phenyldichlorosilane to allyl and methallyl chloride was studied. In the presence of chloroplatinic acid, each of these forms propylene from allyl chloride as well as 3-chloropropyl- and *n*-propylsilane derivatives. With methallyl chloride little or no isobutylene or isobutylsilane derivative forms under the same conditions and excellent yields of 3-chloro-2-methylpropylsilanes are obtained. The preparation and properties of twenty-nine 3-chloroalkylsilicon compounds are described.

The addition of four hydrides of silicon to allyl and methallyl chlorides in the presence of chloroplatinic acid was studied. The four hydrides, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, and phenyldichlorosilane each formed only one adduct, either the 3-chloropropyl- or 3-chloro-2-methylpropylsilane derivatives with allyl or methallyl chloride. No isomeric adducts such as 2-chloro-1-methylethylsilane were detectable.

Some of the compounds described in this paper have been reported previously. Sommer, *et al.*,[1] separated 3-chloropropyltrichlorosilane from a mixture obtained by chlorination of propyltrichlorosilane. More recently, Wagner[2] reported the synthesis of this compound from trichlorosilane and allyl chloride in 51% yield in the presence of platinized carbon at 160–166° in an autoclave. Wagner found propyltrichlorosilane and tetrachlorosilane as by-products.

Petrov[3] apparently had difficulties with this system and reported that under essentially the

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(1) L. H. Sommer, E. Dorfman, G. H. Goldberg and F. C. Whitmore, THIS JOURNAL, **68**, 488 (1946).

(2) G. H. Wagner, U. S. Patent 2,637,738, May 5, 1953.

(3) A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov and G. V. Odabashyan, *Izvestia Akad. Nauk. S.S.S.R.*, **10**, 1206 (1957).