than that of the synthetic optically inactive form with the double bond conjugated to the benzene ring. The hexahydrocannabinols have less marihuana activity. Comparative pharmacological values with that of a highly potent product obtained by Dr. J. C. Matchett through fractionation of purified red oil in a molecular still and used as a standard by Dr. S. Loewe at the Cornell Medical School in tests according to his procedure of "Bioassay by Approximation" (*J. Am. Pharm. Assoc.*, **28**, 427 (1939); *J. Pharm. Exptl. Therap.*, **66**, 23 (1939)) are shown in Table I.

TABLE I

BIOASSAY OF TETRAHYDRO AND HEXAHYDRO CANNABINOLS

Substance	Min. Potency above	Max. Potency below	Mean value potency max. deviation
Standard red oil	....	....	1.00
Cannabidiol	....	....	0.00
Tetrahydrocannabinol, −165°	1.50	2.80	2.15 ± 0.66
Tetrahydrocannabinol, −240°	1.50	2.00	1.75 ± .25
Hexahydrocannabinol, −70°	0.60	0.80	0.70 ± .10
Tetrahydrocannabinol (syn.)	.13	.27	.20 ± .07
Hexahydrocannabinol (syn.)	.10	.20	.15 ± .05

The acetates and methyl ethers of the two tetrahydrocannabinols were colorless, highly viscous oils. Tetrahydrocannabinol $[\alpha]^{34}\text{D}$ −164° gave an acetate $[\alpha]^{34}\text{D}$ −167° and methyl ether $[\alpha]^{32}\text{D}$ −166°; tetrahydrocannabinol $[\alpha]^{30}\text{D}$ −240° gave an acetate $[\alpha]^{34}\text{D}$ −229° and methyl ether $[\alpha]^{32}\text{D}$ −226°.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
IN COLLABORATION WITH THE
TREASURY DEPARTMENT
NARCOTICS LABORATORY
WASHINGTON, D. C.

ROGER ADAMS
S. LOEWE
D. C. PEASE
C. K. CAIN
R. B. WEARN
R. B. BAKER
HANS WOLFF

RECEIVED AUGUST 13, 1940

HINDERED INTERNAL ROTATION OF METHYL GROUPS: THE ENTROPY OF SILICON TETRAMETHYL

Sir:

We have recently completed an investigation which indicates that the potential hindering internal rotation of methyl groups is probably due to hydrogen repulsions.

A study of the entropy of gaseous silicon tetramethyl yields a potential of 1280 calories, compared to 4800 calories for tetramethylmethane. If the potential were mainly due to lack of cylindrical symmetry in the bond orbitals caused by electron interactions, a higher potential than 4800 calories might be predicted for silicon tetramethyl, due to the large number of electrons. Conclusion of complete calorimetric measurements in this Laboratory down to 12°K. on silicon tetramethyl permits an accurate estimate of the hindering potential. The entropy has been calculated using the following frequencies and distances[1]:

Carbon skeleton: ${}^1\omega_1 = 598$, ${}^2\omega_2 = 202$, ${}^3\omega_{4,5,6} = 239$, ${}^3\omega_{7,8,9} = 800$ cm.$^{-1}$.
CH_3 internal: ${}^4\delta(\pi) = 1264$, ${}^8\delta(\sigma) = 1427$, ${}^4\nu(\pi) = 2905$, ${}^8\nu(\sigma) = 2963$ cm.$^{-1}$.
CH_3 rocking: ${}^8\delta = 950$ cm.$^{-1}$.
Distances: Si–C = 1.93 Å., C–H = 1.09 Å.

The frequency ${}^3\omega_{7,8,9}$ is estimated from the frequencies 696 and 831 cm.$^{-1}$ which are apparently a result of resonance degeneracy. The rocking frequencies are estimated by analogy with ethane. The calculation of the entropy at 227.00°K. and at 299.8°K. (the normal boiling point) is summarized in Table I along with the corresponding calorimetric values.

TABLE I

THE ENTROPY OF SILICON TETRAMETHYL IN THE IDEAL GAS STATE FROM MOLECULAR AND SPECTROSCOPIC DATA

	227.0°K., e. u.	299.8°K., e. u.
Translational and rotational (free)	72.40	75.73
Vibrational (${}^3\omega_{7,8,9}$)	0.23 ± 0.08	0.64 ± 0.1
Vibrational (${}^8\delta = 950$)	.28 ± .08	.85 ± .2
Vibrational (other modes)	7.59	10.59
Total	80.50 ± 0.16	87.81 ± 0.3
Calorimetric	77.94 ± .30	86.33 ± .6
$(S_f - S) \times 4$ (experimental)	2.56 ± 0.46	1.48 ± 0.9
$(S - S) \times 4$ ($V = 1280$, $I = 5.3 \times 10^{-40}$)	2.56	1.73

The heat of vaporization was obtained temporarily from the measured vapor pressure equation and approximate state data. Hence the larger error at the higher temperature where the correction to the gas volume is larger. The potential of 1280 ± 160 calories was obtained from Pitzer's tables[2] to fit the experimental discrepancy, $(S_f - S) \times 4$. At the lower temperature if the 950 frequency were in error by 200 cm.$^{-1}$, and if $\omega_{7,8,9}$ should really be at 696 cm.$^{-1}$, the entropy would only be raised by 0.7 e. u. and the potential would then be 1600 calories.

THE SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

J. G. ASTON
R. M. KENNEDY

RECEIVED AUGUST 23, 1940

---

(1) Rank and Bordner, *J. Chem. Phys.*, **3**, 248 (1935).
(2) Pitzer, *ibid.*, **5**, 469 (1937).