excess of 1.2 e.u. for *n*-hexane over diisopropyl at 49.5 liters.[1]

TABLE I

ENTROPY OF VAPORIZATION

| | $v_g$ = 403 lit. | $t$, °C. | $v^g/v^l$ = 2703 | $t$, °C. |
|---|---|---|---|---|
| $C_7H_{16}$ | 29.5 | 25 | 29.5 | 25 |
| $C_7F_{16}$ | 31.1 | 15 | 32.4 | 7 |
| Diff. | 1.6 | | 2.9 | |

Pitzer[4] has shown that in the case of molecules having radial intermolecular potentials of the same form, such as the rare gases, the entropies of vaporization are equal not at equal vapor volumes, $v^g$, but at equal ratios of vapor to liquid volume, $v^g/v^l$, but Hildebrand and Gilman[5] showed that in the case of polyatomic molecules with different liquid volumes the agreement is considerably better at equal $v^g$. The molal volume of perfluoroheptane is so much larger than that of heptane that a much lower temperature must be taken to make the comparison at equal $v^g/v^l$, 7° if the heptane is at 25°. Table I gives the comparison under these conditions. The difference in this case, 2.9 e.u., is, in our opinion, greater than is reasonable to expect from difference in order alone, and it furnishes another instance of the inferiority of the corresponding states rule as a basis for comparing polyatomic molecular species with potential fields so far from radial.

[4] K. S. Pitzer, *J. Chem. Phys.*, **7**, 583 (1939).

[5] J. H. Hildebrand and T. S. Gilman, *ibid.*, **15**, 229 (1947).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

---

## Correction Concerning Some Reported Derivatives of D-Talitol

BY C. S. HUDSON, M. L. WOLFROM AND T. Y. SHEN

RECEIVED APRIL 10, 1952

Barker and Bourne[1] have recently shown that data of the literature justify a belief that a dimethylene acetal which Hann, Haskins and Hudson[2] reported as 2,4:3,5-dimethylene-D-talitol is in reality the 2,4:3,5-dimethylene-allitol that Wolfrom, Lew and Goepp[3] prepared from authentic allitol. Upon receipt of this information from Messrs. Barker and Bourne by early letter, for which we express our appreciation, we examined the original samples from the two researches[2,3] by mixed melting point measurements and by X-ray diffraction diagrams. In like manner the respective original samples of two derivatives,[2,3] namely, the 1,6-diacetate and the 1,6-ditosylate, were also compared. In all cases the results show unequivocally that the reported "D-talitol" acetal is 2,4:3,5-dimethylene-allitol. In one of the researches[2] three additional derivatives of the acetal were reported as belonging in the D-talitol series; since the acetal is now known to be of the allitol series the names of these derivatives are be changed to 1,6-dibenzoyl-2,4:3,5-dimethylene-allitol (m.p. 188–189°), 1,6-didesoxy-2,4:3,5-dimethylene-allitol (m.p. 165–166°) and 1,6-didesoxy-1,6-diiodo-2,4:3,5-dimethylene-allitol (m.p. 219–220°). All the substances have *meso* configurations and are to be regarded as devoid of optical rotation; the very small specific rotations that were reported[2] are near the limits of observation. The recorded melting points[2,3] are essentially correct.

3016 TILDEN ST., N. W., WASHINGTON, D. C. (C. S. H.)
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO
(M. L. W. AND T. Y. S.)

[1] S. A. Barker and E. J. Bourne, *J. Chem. Soc.*, 905 (1952).

[2] R. M. Hann, W. T. Haskins and C. S. Hudson, THIS JOURNAL, **69**, 624 (1947).

[3] M. L. Wolfrom, B. W. Lew and R. M. Goepp, Jr., *ibid.*, **68**, 1443 (1946).

---

## The Heat of Combustion and Resonance Energy of Tropolone

BY WARD N. HUBBARD, CHARLES KATZ, GEORGE B. GUTHRIE, JR., AND GUY WADDINGTON

RECEIVED APRIL 5, 1952

In 1945, Dewar predicted[1] that tropolone (2,4,6-cycloheptatriene-1-one-7-ol) would exhibit aromaticity and later made a theoretical estimate of its resonance energy.[2] Following its synthesis,[3] Dr. W. von E. Doering of the Hickrill Chemical Research Foundation suggested that an estimate of its resonance energy from heat of combustion data would be valuable and offered four grams of tropolone to this Laboratory. Consequently, and because of current interest in other related seven-membered cyclic compounds (*e.g.*, ref. 3b), heat of combustion measurements for tropolone[4] were included in the Bureau of Mines calorimetric program.

**Material.**—The sample had been prepared and purified according to ref. 3a and was then recrystallized from cyclohexane and sublimed three times. The method of purification and the carbon dioxide determinations (see table) suggest that the material (m.p. 51°) was of high purity. The material was non-hygroscopic and when compressed into briquets was not significantly volatile at room temperature.

**The Apparatus and Its Calibration.**—The apparatus (with the exception of the bomb) and combustion technique have been previously described.[5] The bomb used in this investigation was sealed with a pure gold gasket and had an internal volume of 0.374 l. The energy equivalent of the calorimeter was determined by combustion of benzoic acid (National Bureau of Standards Standard Sample 39g) having for its isothermal heat of combustion at 25° a value of $-\Delta U_B/M$ of 26.4338 abs. kj. g.$^{-1}$. Since the conditions in these experiments were not quite those of the standard bomb process, the N.B.S. value was corrected to 26.4306 abs. kj. g.$^{-1}$. Eight combustions of benzoic acid yielded an average value 3190.95 cal. deg.$^{-1}$ for the energy equivalent, $S_B$, of the system. The average deviation from the mean of these experiments was ±0.006% with a maximum spread of 0.025%.

**Auxiliary Quantities.**—Weights were corrected to a vacuum basis by use of a density value of 1.34 g. cc.$^{-1}$ for

---

[1] M. J. S. Dewar, *Nature*, **155**, 50, 141, 451 (1945).

[2] M. J. S. Dewar, *ibid.*, **166**, 790 (1950).

[3] (a) W. von E. Doering and L. H. Knox, THIS JOURNAL, **72**, 2305 (1950); (b) **73**, 828 (1951); (c) J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *Chemistry and Industry*, 427 (1950); (d) R. D. Haworth and J. D. Hobson, *ibid.*, 441 (1950).

[4] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 503 (1951), have recently published a value of the heat of combustion of tropolone having a claimed accuracy of ±0.9 kcal./mole. This datum was obtained for them by G. R. Nicholson of Imperial Chemical Industries Limited. Because of the higher order of accuracy of the present work and because of the current great interest in tropolone, it has seemed desirable to record both the original and derived data of the combustion experiments performed in this Laboratory.

[5] W. N. Hubbard, J. W. Knowlton and H. M. Huffman, THIS JOURNAL, **70**, 3259 (1948).