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.

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

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

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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.

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(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).

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The Heat of Combustion and Resonance Energy of Tropolone

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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

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(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).

tropolone estimated from the dimensions and mass of the briquets. The specific heat of tropolone, used in calculating the heat capacity of the bomb contents, was estimated to be 0.29 cal. deg.$^{-1}$. The heats of formation of water and carbon dioxide at 25° were taken to be −68,317.4[6] and −94,051.8[7] cal. mole^{-1}, respectively. The correction for the amount of nitric acid formed during combustion was calculated using −13.82[8] kcal. mole^{-1} for the heat of reaction (1) at 25° in the bomb process. For computing the heat of

$$1/2N_2(g) + 5/4O_2(g) + 1/2H_2O(l) + aq \longrightarrow HNO_3(aq) \quad (1)$$

combustion of gaseous tropolone the heat of sublimation at 25° was taken as 20.0 ± 0.2 kcal./mole.[4]

Experimental Data and Discussion of Results.—The data of the four combustions attempted are given in Table I.

TABLE I

1 cal. = 4.1840 abs. joules; mol. wt. tropolone = 122.118

Mass of sample (vac.), g.	q_{fuse}	q_{HNO_3}	Temperature rise, °C.	CO_2 found, % theor.	$-\Delta U_B/M_{(25°)}$, cal. g.$^{-1}$	$\Delta H°_{c\,(25°)}$, kcal. mole^{-1}
0.96941	17.05	0.68	2.01155	99.98_2	6608.7	
.96436	16.74	1.08	2.00095	....	6607.8	−806.06
.96461	16.74	1.00	(2.00082)	99.97_9	(6605.9)	
.96478	15.49	0.77	2.00144	99.99_2	6608.1	−806.10

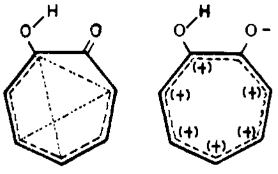
The columns headed q_{fuse} and q_{HNO_3} give the corrections for the combustion of the fuse and the formation of nitric acid; $-\Delta U_B/M$ is the heat evolved in the bomb process; and ΔH_c° is the heat of combustion of solid tropolone with all the reactants and products in their respective standard states. In each experiment the ignition energy was 1.28 cal.; the Washburn correction was -0.063% ΔU_B; and the heat capacities of the initial and final contents of the bomb, S_I and S_F were 3.10 and 3.34 cal. deg.$^{-1}$, respectively. The bomb gases were tested for carbon monoxide following two of the combustions. In each case the tests showed less than 0.00007% carbon monoxide present. The calorimetry of the third experiment was somewhat uncertain and the result is given no weight. The small value of q_{HNO_3} in the first experiment suggests that possibly some of the nitric acid formed was lost. Therefore $-\Delta U_B/M$ for this combustion may be 0.4 to 0.7 cal. g.$^{-1}$ too high. The average heat of combustion, ΔH_c°, of the remaining two experiments is −806.08 kcal. mole^{-1}. From this, the standard heat of formation, ΔH_f° (25°), of tropolone from graphite, hydrogen and oxygen is calculated to be −57.23 ± 0.2 kcal. mole^{-1} for the solid and −37.23 ± 0.3 kcal. mole^{-1} for the gas.

The resonance energy of tropolone has been calculated and discussed by Cook, *et al.*,[4] and by Koch.[9] These two discussions are weakened by logical inconsistency; namely, the resonance energy of tropolone calculated by Coates and Sutton's[10] bond energies has been compared with resonance energies calculated both from heat of combustion data using Pauling's bond energies and from heat of hydrogenation data. In any discussion of resonance it is desirable that all resonance energies used be calculated on a common basis so that uncertainties in the bond energies and related quantities tend to cancel.

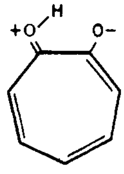
Since most of the resonance energies based on Pauling's bond energies needed for this discussion are readily obtained, and since many chemists are more familiar with these, the resonance energy of tropolone has been recalculated. Using Pauling's table of bond energies,[11] the heat of formation calculated for the reference structure of gaseous tropolone is −1.4 kcal. mole^{-1}. Therefore, tropolone is 36 kcal. mole^{-1} more stable than the reference structure. This is 7 kcal. mole^{-1} greater than the value 29 kcal. mole^{-1}, reported by Cook, *et al.*,[9] and the difference arises from the differences between the two sets of bond energies used in the two calculations.

Koch[10] has estimated from an investigation of the infrared spectrum that a hydrogen bond between the hydroxyl and carbonyl group stabilizes tropolone by 7 kcal. mole^{-1}. This value may be a little high; a more conservative estimate would be 5–7 kcal. mole^{-1}. On the other hand, electron and X-ray diffraction studies[12] indicate that tropolone is planar. Ring strain probably destabilizes tropolone by 4–5 kcal. mole^{-1}. Thus, the resonance energy of tropolone is 33–36 kcal. mole^{-1}.

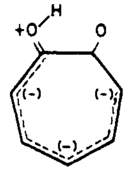
All the structures with one formal bond (or charge separation) that can be written for tropolone correspond to those which would be written for (a) tropone (cycloheptatrienone), (b) the vinylog of the carboxylic acids and (c) phenol. Since the resonance energy of tropone has not been determined, an estimate of 16–24 kcal./mole[13] will be used. The resonance energy of the carboxylic acids is 24–28 kcal./mole^{-1}. The phenol-like struc-



(A)



(B)



(C)

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[6] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bureau Standards*, **34**, 143 (1945).

[7] E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

[8] E. J. Prosen and F. D. Rossini, *ibid.*, **33**, 255 (1944).

[9] H. P. Koch, *J. Chem. Soc.*, 513 (1951).

[10] G. E. Coates and L. E. Sutton, *ibid.*, 1187 (1948).

[11] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 54.

[12] J. M. Robertson, *J. Chem. Soc.*, 1222 (1951); K. Hedberg and E. Heilbronner, THIS JOURNAL, **73**, 1386 (1951).

[13] This estimate is reached as follows: Two sets of structures may be written, each corresponding to a linear system of four conjugated double bonds. Pauling has estimated (as quoted in ref. 9) that four conjugated carbon–carbon double bonds have a resonance energy of 17 kcal. mole. Wheland (ref. 15) suggests 18 kcal. mole^{-1}. Since there are two sets of these structures the resonance energy may be 6 kcal. mole^{-1} greater, *i.e.*, total resonance energy 24 kcal. mole^{-1}. *o*-Benzoquinone, which has two hetero-atoms and structures analogous to tropone, has a resonance energy of 16 kcal. mole^{-1}. The resonance energy of tropone probably lies between these two limits.

tures probably do not make a significant contribution.[14]

Application of a crude method of calculating resonance energies suggested by Wheland[15] shows that the resonance energy of tropolone should be less than the sum (40–52 kcal. mole^{-1}) of the resonance energies of these two hybrid structures. This calculation gives 24 kcal. mole^{-1} for the resonance energy of tropone, 24 kcal. mole^{-1} for the carboxylic acid vinylog and 30 kcal. mole^{-1} for tropolone. Although this calculation is not intended for non-hydrocarbons, it shows clearly the effect of superimposing two resonance hybrids. The observed resonance energy (36 kcal. mole^{-1}) is quite reasonable for a hybrid of the tropone and carboxylic acid vinylog structures.

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[14] In phenol these structures account for a 7 kcal. mole^{-1} increase in the resonance energy over that of benzene. These structures (c) are certainly less important than structure (b) since the cycloheptatriene nucleus is a poorer electron acceptor than the carbonyl group or a phenyl group.

[15] G. W. Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 79 *ff.*

CONTRIBUTION NO. 29 FROM
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Reactions of Pivalyl, 2-Thenoyl and 2-Furoyl Chlorides with Cyclopentene[1]

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RECEIVED SEPTEMBER 17, 1951

Treatment of a mixture of pivalyl chloride and cyclopentene in carbon disulfide with anhydrous stannic chloride (as catalyst) and subsequent dehydrohalogenation of the intermediate product by means of refluxing diethylaniline yielded an impure oil which reacted further with 2,4-dinitrophenylhydrazine to give a crystalline compound assigned the structure of 1-pivalylcyclopentene 2,4-dinitrophenylhydrazone. This structure was further substantiated by observation of the ultraviolet absorption spectrum of the oil which exhibited an intense maximum at 239 mμ (*E* 1.55, *c* 150 mg./liter) and a much weaker one at *ca.* 310 mμ (*E* 0.02) characteristics of an α,β-unsaturated ketone with two alkyl substituents variously attached to the available positions on the α- and β-carbons.[3] The oil proved to be inactive as an antibiotic[4] in *in vitro* tests with Gram-negative *E. coli* and Gram-positive *B. mycoides*.

Reaction of 2-thenoyl chloride with cyclopentene according to the procedure used with pivalyl chloride or with substitution of phosphorus pentoxide for the stannic chloride gave small amounts of 2-thenoic acid as the only isolable product, while use of anhydrous aluminum chloride as the catalyst gave excessive condensation to produce a small amount of yellow non-acidic crystalline material for which elemental analyses indicated the empirical formula $C_{13}H_{14}O_2S$. Anhydrous antimony pentachloride, a Lewis acid of strength intermediate between that of aluminum chloride and stannic chloride,[5] however, produced a small yield of an unstable oil which gave a positive isatin test and formed a crystalline derivative (with 2,4-dinitrophenylhydrazine reagent) of composition corresponding to that expected for 1-(2-thenoyl)-cyclopentene 2,4-dinitrophenylhydrazone.

With 2-furoyl chloride and cyclopentene, stannic chloride gave at least termolecular condensation to a colorless crystalline product of empirical formula $C_{14}H_{16}O_3$ which showed a positive pine splinter test for the presence of the furan nucleus.

Experimental[6]

Reaction of Pivalyl Chloride.[7]—A solution of 42 g. (0.161 mole) of anhydrous stannic chloride in 100 ml. of purified[8] carbon disulfide was cooled to −15° and treated with a solution of 11 g. (0.162 mole) of cyclopentene and 21.3 g. (0.177 mole) of pivalyl chloride, added dropwise with stirring. After one additional hour of stirring and four more hours in a refrigerator the viscous mixture (which had changed from light yellow to black during the course of reaction) was poured onto crushed ice and stirred to decompose the complex present. The organic layer was separated, washed with water, dried and evaporated. The resultant residue was refluxed for five hours at 185° with 20 ml. (0.125 mole) of purified[9] diethylaniline. The cooled mixture was diluted with ether, washed successively with excess 5% hydrochloric acid and 5% aqueous sodium hydroxide, dried, evaporated and fractionally-distilled; yield 7.7 g. of faintly yellow liquid, b.p. 63–68° (7 mm.), not obtained analytically pure. Treatment of a portion of this liquid with 2,4-dinitrophenylhydrazine[10] gave **1-pivalylcyclopentene 2,4-dinitrophenylhydrazone**, crystallizing from alcohol in yellow-orange needles, m.p. 144°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.07; N, 16.85. Found: C, 57.81; H, 6.02; N, 16.87.

The ultraviolet absorption spectrum of another portion of the yellow liquid was determined by means of a Beckman quartz spectrophotometer, model DU, using matched silica cells of 1-cm. path length and absolute methanol as a solvent. The oil obeyed Beer's law in the range 15–1500 mg./liter tested.

A third portion was used for tests on antibacterial activity by means of the agar diffusion method.[11] Solutions of 1–100 mg. of the oil in 0.3 ml. of methanol showed no apparent inhibition of growth for either *Escherichia coli* or *Bacillus mycoides*.

Reaction of 2-Thenoyl Chloride.—A mixture of 6 g. (0.088 mole) of cyclopentene, 13.5 g. (0.092 mole) of 2-thenoyl chloride, and 100 ml. of purified[8] carbon disulfide was cooled to 0° in a flask fitted with a calcium chloride drying tube and was treated slowly, with stirring, with 26.6 g. (0.089 mole) of anhydrous antimony pentachloride. The brown solution was stirred 30 minutes longer and then poured into a mixture of crushed ice and concentrated hy-

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[1] From the Ph.D. thesis of Theodore Largman.

[2] Dept. of Chemistry, University of Oregon, Eugene, Oregon.

[3] R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941). Compare data for 1-acetylcyclopentene, I. Heilbron, *et al.*, *J. Chem. Soc.*, 1827 (1949).

[4] For data and theories on the antibacterial action of α,β-unsaturated ketones see W. B. Geiger and J. E. Conn, THIS JOURNAL, **67**, 112 (1945); H. Rinderknecht, *et al.*, *Biochem. J.*, **41**, 463 (1947).

[5] O. C. Dermer, *et al.*, THIS JOURNAL, **63**, 2881 (1941). See also K. Bodendorf and H. Böhme, *Ann.*, **516**, 1 (1935); N. O. Calloway, *Chem. Revs.*, **17**, 327 (1935).

[6] Microanalyses were performed by B. Jarvis and A. Rosen. Melting points were determined by means of an Eimer and Amend melting point block and are uncorrected.

[7] Preparative procedure adapted from that of R. Robinson and co-workers, *J. Chem. Soc.*, 1285 (1935); 763 (1936), for 1-acetylcyclopentene.

[8] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 365.

[9] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 550.

[10] Procedure of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

[11] S. A. Waksman, "Microbial Antagonisms and Antibiotic Substances," 2nd Ed., The Commonwealth Fund, New York, N. Y., 1947 p. 75.