[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA]

The Thermodynamics of Styrene and its Methyl Derivatives[1]

BY CHARLES W. BECKETT[2] AND KENNETH S. PITZER[3]

In the preceding paper[4] are given the data necessary to calculate the thermodynamic properties of styrene in the perfect gas state. By making use of the increments for the addition of a methyl group to toluene[5] or to propylene[6] one may estimate values for the methyl styrenes.

Styrene.—The thermodynamic properties of styrene, calculated from data given in the preceding paper,[4] are shown in Table I. The uncertainty of these values is estimated to be about 0.5 cal./deg. mole at the lower temperatures. It may be somewhat larger at the higher temperatures. These calculated values agree fairly well with the meager amount of independent data available. The single observed heat capacity given by Scott and Mellors[7] is $C_p^0 = 35.83$ and C_p^0 cor. $= 36.16$ at 100°. The calculated value at this temperature is 35.91 ± 0.50.

TABLE I

CALCULATED THERMODYNAMIC PROPERTIES OF STYRENE IN THE IDEAL GASEOUS STATE, CAL./DEG. MOLE

Temp., °K.	C_p^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S
298.16	29.18	16.72	65.76	82.48
300	29.35	16.79	65.86	82.65
400	38.32	21.07	71.28	92.35
500	45.94	25.32	76.44	101.76
600	52.14	29.28	81.42	110.70
700	57.21	32.93	86.21	119.14
800	61.40	36.22	90.82	127.03
900	64.93	39.22	95.26	134.48
1000	67.92	41.95	99.54	141.49
1100	70.48	44.44	103.66	148.09
1200	72.66	46.70	107.61	154.31
1300	74.54	48.77	111.44	160.20
1400	76.16	50.67	115.13	165.79
1500	77.57	52.42	118.68	171.09

The heat of formation of styrene at 0°K. in the ideal gaseous state is

$$\Delta H_{f0}^0 = 40.34 \pm 0.30 \text{ kcal./mole}$$

This value was obtained from the following: the heat content function at 298.16°K. in Table I, the heat of vaporization[4] (10.50 ± 0.10 kcal./mole at 298.16°K.), the heat of formation of liquid styrene,[8] and the heat contents of graphite and hydrogen at 298.16°K.[9]

Combining the above value of ΔH_{f0}^0 for styrene with that for ethylbenzene[5] gives ΔH_0^0 equal to 26.42 ± 0.40 for the dehydrogenation of ethylbenzene to styrene. If this is combined with the heat content functions of these compounds[5] and with that of hydrogen,[9] the heat of dehydrogenation at 355°K. is 28.38 ± 0.40 kcal./mole as compared to the value, 28.56 ± 0.25, from hydrogenation data.[10]

Equilibrium constants for the dehydrogenation of ethylbenzene, calculated from the free energy functions using ΔH_0^0 equal to 26.42, are about 25 per cent. less than the experimental constants at 360 to 495° published recently by Ghosh.[11] This discrepancy is near the estimated limits of error in ΔH_0^0 and $(F^0 - H_0^0)/T$. Since experimental details were not given, the uncertainty of the observed equilibrium constants cannot be appraised.

Methyl Styrenes.—The thermodynamic functions of some of the methyl styrenes were estimated by the method of increments.[5,6] Thus, the entropy of *p*-methylstyrene is

$$S\,(p\text{-methylstyrene}) = S\,(\text{styrene}) + S\,(p\text{-xylene}) - S\,(\text{toluene}) + R \ln 2$$

and that of *trans*-β-methylstyrene is

$$S\,(trans\text{-}\beta\text{-methylstyrene}) = S\,(\text{styrene}) + S\,(trans\text{-2-butene}) - S\,(\text{propylene}) + R \ln 2$$

The equations for the other properties have the same form except that the last term, $R \ln 2$, is omitted in the heat content function and heat capacity. This term is merely an adjustment of the symmetry number.

The estimated properties for *m*-methylstyrene are the same as those given for *p*-methylstyrene except that the quantity $R \ln 2$ is added to S and to $-(F^0 - H_0^0)/T$ in order to take into account the lower symmetry number of the meta compound. This is in accord with the small difference, apart from the symmetry numbers, between properties of meta and para xylenes.[5]

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(1) This work was performed at the University of California as part of the work of the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons" with headquarters at the National Bureau of Standards.

(2) Research Associate on the American Petroleum Institute Research Project 44.

(3) Associate Supervisor on the American Petroleum Institute Research Project 44.

(4) K. S. Pitzer, L. Guttman and E. F. Westrum, Jr., THIS JOURNAL, **68**, 2209 (1946).

(5) K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943); W. J. Taylor, D. D. Wagman, M. A. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

(6) J. E. Kilpatrick and K. S. Pitzer, *J. Research, Natl. Bur. Standards*, **37**, 163 (1946).

(7) R. B. Scott and J. W. Mellors, *ibid.*, **34**, 243 (1945).

(8) E. J. Prosen and F. D. Rossini, *ibid.*, **34**, 59 (1945).

(9) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

(10) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, THIS JOURNAL, **59**, 831 (1937).

(11) J. C. Ghosh, S. Ran Das Guha and A. N. Roy, *Current Sci.*, **14**, 269 (1945).

The method of increments is a fairly reliable approximation for these compounds. The over-all uncertainty of these estimates may exceed one cal./deg. mole, but the uncertainty of their differences probably is much less.

The method of increments, however, is not reliable for the other methyl derivatives in which steric effects are large and specific in character. A consideration of these steric effects indicates that the properties of *o*-methyl, α-methyl and *cis*-β-methylstyrene are about the same as those given for *p*-methylstyrene. This estimate is considered the best one possible at this time.

TABLE II

ESTIMATED THERMODYNAMIC PROPERTIES OF *p*-METHYLSTYRENE IN THE IDEAL GASEOUS STATE, CAL./DEG. MOLE

Estimates for the *o*-, *m*-, α- and *cis*-β-methylstyrenes are the same except that $R \ln 2$ (1.4) should be added to the entropy and the $-(F^0 - H_0^0)T$ function of *m*-methylstyrene.

Temp., °K.	C_p^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S
298.16	34.7	20.3	71.4	91.7
300	34.9	20.3	71.5	91.9
400	44.8	25.2	78.1	103.3
500	53.5	30.0	84.2	114.3
600	60.7	34.6	90.1	124.7
700	66.8	38.8	95.8	134.5
800	71.8	42.6	101.2	143.7
900	76.1	46.1	106.4	152.5
1000	79.8	49.3	111.4	160.7
1100	82.9	52.2	116.3	168.4
1200	85.6	54.9	120.9	175.7
1300	87.9	57.3	125.4	182.7
1400	89.9	59.6	129.7	189.3
1500	91.6	61.6	133.9	195.5

TABLE III

ESTIMATED THERMODYNAMIC PROPERTIES OF *trans*-β-METHYLSTYRENE IN THE IDEAL GASEOUS STATE, CAL./DEG. MOLE

Temp., °K.	C_p^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S
298.16	34.9	19.9	71.0	90.9
300	35.1	20.0	71.1	91.1
400	45.2	25.1	77.6	102.6
500	54.0	30.0	83.7	113.7
600	61.2	34.6	89.6	124.2
700	67.2	38.9	95.3	134.1
800	72.2	42.7	100.7	143.4
900	76.4	46.2	105.9	152.2
1000	80.0	49.5	111.0	160.4
1100	83.1	52.4	115.8	168.2
1200	85.8	55.1	120.5	175.5
1300	88.1	57.5	125.0	182.5
1400	90.0	59.8	129.4	189.1
1500	91.7	61.8	133.5	195.4

Summary

Thermodynamic properties of styrene were calculated. Estimates were given for the properties of the various methyl styrenes.

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α-(Dialkylaminomethyl)-2-phenyl-4-quinolinemethanols with 8-Amino or Hydroxy Substituents[1]

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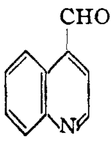
King and Work[2] have reported that the simple quinine analogs, α-(dialkylaminomethyl)-4-quinolinemethanols (I), are suppressive agents for certain forms of avian malaria. These compounds are less active and less toxic than 8-aminoquinolines of the Plasmochin type (II), which have a different mode of action on the malaria parasite.[3] In the search for superior antimalarial drugs sponsored by the Committee on Medical Research, it was considered of interest to investigate the properties of compounds containing both α-(dialkylaminomethyl)-4-quinolinemethanol and 8-amino groups. Earlier work had shown that a 2-phenyl substitutent greatly enhances antimalarial activity in 4-quinolinemethanols and diminishes it in 8-aminoquinolines.[3] Both series of drugs (I and II) include highly active compounds which do not contain the 6-methoxy group present in quinine and Plasmochin.[3]



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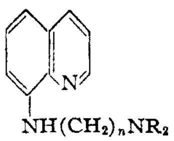

II

This paper reports the synthesis of 8-amino King–Work types, III, which contain a 2-phenyl substituent and are unsubstituted in the 6-position. The corresponding 8-hydroxy com-

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[1] The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the Massachusetts Institute of Technology.

[2] King and Work, *J. Chem. Soc.*, 1307 (1940); 401 (1942); see Kaufmann, *Ber.*, **46**, 1823 (1913); Rabe, Pasternack and Kindler, *ibid.*, **50**, 144 (1917).

[3] Pharmacological and clinical characteristics of the various classes of antimalarial drugs will be described in a forthcoming monograph by the Survey of Antimalarial Drugs.