768. *The Entropies of Alkyl Radicals.*

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Detailed calculations of the standard entropies of methyl, ethyl, propyl, and isopropyl radicals over the temperature range 200—1000°K are described. The entropies of the propyl and isopropyl radicals have not previously been calculated, and the data presented for methyl and ethyl represent a refinement of earlier values.

Mutually consistent molecular models have been used throughout. A simple approximation method is described for the calculation of the standard entropies of any large primary n-alkyl radical at high temperatures. Such entropies are unlikely to be in error by more than 1 e.u.

THE literature contains several accounts of statistical mechanical calculations of standard entropies of methyl [1-4] and ethyl [3] radicals. The stimuli for such calculations are the impracticability of thermal measurements on these systems, and the utility of the information in kinetic studies. As in this instance, the resulting entropies are often intended for the calculation of equilibrium constants or of the ratios of the pre-exponential factors for opposing reactions. Estimates of the entropies of these radicals have also been used for transition state calculations.[2,3]

Provided that there are no low-lying excited electronic states of the radical, and that the multiplicity of the ground electronic state is known, translational and electronic contributions to the entropy may be calculated with high precision. The parameters which determine the vibrational and rotational contributions to the entropy are, with a few exceptions,[5] matters for conjecture. However, since translation usually provides the major contribution, the total entropy is relatively insensitive to the choice of rotational and vibrational parameters.

No estimates of the entropies of radicals larger than ethyl are available, and these are now needed. In addition, spectroscopic data for methyl, now available,[5] allow more precise estimates of the rotational and vibrational parameters for this and other alkyl radicals. It seems worthwhile, therefore, to calculate the entropies of n-alkyl radicals in such a way as to introduce a degree of mutual consistency in the models used, and to base these models upon the most recent experimental data. In many cases of kinetic interest, mutual consistency of calculated radical entropies is likely to produce a marked reduction in the uncertainties associated with the subsequent calculation of equilibrium constants and rate parameters. The present calculations might therefore be expected to be more useful for the testing of experimental data and the prediction of rate parameters.

Method.—Translational entropies were calculated for an ideal gas in a standard state of one atmosphere using the atomic weights and numerical form of the Sackur–Tetrode equation given by Rossini *et al.*[6] An electronic entropy term of $R \ln 2$ was included for all the radical entropies calculated here, but nuclear spin contributions were omitted.

The rotational entropy of methyl, the only rigid system discussed here, was evaluated directly from the equation given by Rossini *et al.*[6] The entropy contributions for the total rotations of the other radicals were calculated by using Kassel's extension [7] of the method of Eidinoff and Aston [8] for non-rigid systems. In the case of propyl one of the internal tops, $-CH_2\cdot$, is not symmetric, and the integration over all configurations of this top was

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[1] Zeise, *Z. Elektrochem.*, 1942, **48**, 693.
[2] Bywater and Roberts, *Canad. J. Chem.*, 1952, **30**, 773.
[3] Ree, Ree, Eyring, and Fueno, *J. Chem. Phys.*, 1962, **36**, 281.
[4] J.A.N.A.F., "Thermochemical Tables," Dow Chemical Co., Midland, Michigan, 1960.
[5] Herzberg, *Proc. Roy. Soc.*, 1961, *A*, **262**, 291.
[6] Rossini *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Pittsburgh, 1953.
[7] Kassel, *J. Chem. Phys.*, 1936, **4**, 276.
[8] Aston and Eidinoff, *J. Chem. Phys.*, 1935, **3**, 379.

carried out numerically. Entropies calculated by Kassel's method refer to unhindered rotation of internal tops; where necessary, corrections for the hindering of internal rotations were applied using the method of Pitzer and Gwinn.[9] Internal interactions between the two tops in propyl and in isopropyl were neglected and these calculations are therefore subject to the same restrictions that Pitzer and Gwinn [9] discuss in relation to the internal rotations of propane.

Vibrational entropies were calculated by the group frequency method,[10] all the vibrations being assumed to be simple harmonic. The limitations of this assumption are discussed in a later section. The entropy contributions of each vibration at each temperature were read off from large scale graphs of the entropy of a harmonic oscillator as a function of $\bar{\nu}/T$.

Model.—General. The fundamental constants and atomic weights used were those listed by Rossini *et al.*[6] Tetravalent carbon atoms were assumed to form valencies regularly tetrahedral in every case. Carbon atoms carrying odd electrons were assumed to form valencies planar and regular trigonal in nature, as Herzberg observed for methyl.[5] The following bond lengths were used throughout: H–C (sp^3), 1·107*A* (as in ethane [11]); H–C (sp^2), 1·08*A* (as in methyl [5]); C(sp^3)–C(sp^3), 1·536*A* (as in ethane [11]); C(sp^2)–C(sp^3), 1·507*A* (as in propene).[12]

Group frequencies for sp^3 hybridised carbon atoms were estimated from the corresponding frequency assignments for ethane [13] giving (in cm.$^{-1}$):

(*a*) for $-CH_3$; 2960 (3), 1440 (3), 990 (2); (*b*) for $>CH_2$; 2960 (2), 1440 (2), 990 (2).

The in-plane vibration frequencies of methyl were calculated from the valence force field secular equation given by Herzberg [13] for planar XY_3 molecules, the force constants which describe the in-plane vibrations of ethylene being used.[13]

The in-plane group frequencies for sp^2 hybridised carbon atoms in other radicals, however, were estimated from the corresponding frequencies of ethylene, giving (in cm.$^{-1}$):

(*c*) for $-\dot{C}H_2$; 3100 (2), 1390 (1), 980 (1); (*d*) for $>\dot{C}H$; 3100 (1), 1300 (1);

the last frequency being chosen by analogy with the vibrational assignment for propene.[14] The out-of-plane vibration frequencies of sp^2 hybridised carbon atoms were calculated from the valence force field secular equation given by Herzberg [13] for XYZ_2 molecules. It was assumed throughout that the same force constant determines the frequency of this motion for all radicals, including methyl, the frequency of which has been estimated as 580 cm.$^{-1}$ from spectroscopic observations.[5]

The skeletal frequencies were calculated from the secular equations for the corresponding di- or tri-atomic systems.[13] Pitzer's recommended force constants were used,[10] with the exception that the C(sp^3)–C(sp^2) bond was assumed to be somewhat stiffer than the normal C–C single bond; a stretching force constant of $4{\cdot}5 \times 10^5$ dyne. cm.$^{-1}$ being assumed by analogy with propene.[14]

The detailed vibrational models for the radicals were (in cm.$^{-1}$):

(i) methyl; 3100 (2), 2930, 1230 (2); 580;
(ii) ethyl; 3100 (2), 2960 (3), 1440 (3), 1390, 1050, 990 (2), 980, 485;
(iii) propyl; 3100 (2), 2960 (5), 1440 (5), 1390, 1100, 990 (4), 980, 960, 460, 380;
(iv) isopropyl; 3100, 2960 (6), 1440 (6), 1300, 1200, 990 (4), 950, 398, 367.

The following symmetry numbers were used for the total rotations; methyl, 6; ethyl, 6; propyl, 6; isopropyl, 18. The rotation of the $-CH_3$ tops of ethyl and of propyl were

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[9] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.
[10] Pitzer, *Chem. Revs.*, 1940, **27**, 39.
[11] Almenningen and Bastiansen, *Acta Chem. Scand.*, 1955, **9**, 815.
[12] Bernstein, *Trans. Faraday Soc.*, 1961, **57**, 1649.
[13] Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1945.
[14] Wilson and Wells, *J. Chem. Phys.*, 1941, **9**, 319.

assumed to be hindered by a threefold cosine barrier of height 3400 cal. mole^{-1}, the figure used by Pitzer for the corresponding motion of n-alkanes.[15] The two $-CH_3$ tops of isopropyl were each assumed to be hindered by a threefold cosine barrier of height 1980 cal. mole^{-1}, the value deduced for the barrier height of propene.[16] The rotations of $-CH_2\cdot$ tops were in all cases assumed to be unhindered, as would be expected if each hydrogen atom of the $-CH_2\cdot$ top were acted upon *independently* by a threefold cosine barrier.

Large primary n-alkyl radicals. For radicals larger than propyl the complete statistical calculation becomes prohibitively complex. Here we describe an alternative approach, which involves an estimation of the difference between the standard entropies of a primary n-alkyl, R•, and the parent n-alkane, RH. These entropy differences may be attributed to the following differences in molecular structure:

(i) differences in molecular weight;

(ii) differences between the products of the three principal moments of inertia when both the primary n-alkyl and the n-alkane are treated as *rigid* molecules;

(iii) differences between the overall symmetry numbers when the two systems are treated as *rigid* molecules;

(iv) the electronic entropy term, characteristic of the radical only;

(v) when the radical and the alkane are treated as *non-rigid* systems they differ in that the former contains a freely rotating internal top $-CH_2\cdot$ and the latter a top, $-CH_3$, undergoing rotation against a threefold barrier of height 3400 cal. mole^{-1};

(vi) the alkane possesses a set of group vibration frequencies attributable to one of the terminal $-CH_3$ groups, which in the primary n-alkyl are replaced by those associated with the terminal $-CH_2\cdot$ group;

(vii) differences in carbon skeletal frequencies.

The entropy difference due to the difference in molecular weight is 0·047 e.u. at all temperatures for butyl and is even smaller for larger radicals. Similarly the entropy difference due to (ii) is small and decreases as the size of the radical increases. Finally, carbon skeletal frequency differences cannot be calculated with sufficient accuracy to merit the inclusion of the corresponding entropy effects in the subsequent calculations. Entropy differences resulting from factors (i), (ii), and (vii) are therefore not considered further.

The computations can thus be reduced to the evaluation of a quantity δ defined by the relation

$$\delta \equiv R \ln 2 + R \ln 2 + \Delta S_R + \Delta S_V,$$

the terms on the right hand side of the identity being attributable to factors (iii), (iv), (v), and (vi), respectively. The quantity ΔS_R may be further broken down into terms corresponding to the differences in the *internal* symmetry numbers, the axial moments of the tops, and the potential barrier hindering rotation. Thus

$$\Delta S_R = R \ln \frac{3}{2} - \frac{R}{2} \ln \left(\frac{3{\cdot}294}{1{\cdot}764}\right) + (S_f - S)$$

where $(S_f - S)$ is the correction for the hindering of a $-CH_3$ rotation by a threefold barrier of height 3400 cal. mole^{-1}, as calculated by the method of Pitzer and Gwinn.[9]

ΔS_V is the difference between the total entropy contributions of the group vibrations for $-CH_2\cdot$ as calculated for propyl and the corresponding quantities for $-CH_3$.

The approach outlined here overlooks the point, made clear in the work of Aston and Eidinoff,[8] that internal rotations of non-symmetric tops are not separable. However, experience with the complete statistical calculation for propyl indicates that the errors involved in assuming separability are likely to be small. Values of δ as a function of T are listed in Table 2.

It is clear that for very large primary n-alkyl radicals, δ is an approximation to the

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[15] Pitzer, *Ind. Eng. Chem.*, 1944, **36**, 829.

[16] Lide and Mann, *J. Chem. Phys.*, 1957, **27**, 868.

quantity, $S^\circ(\mathrm{R}\cdot) - S^\circ(\mathrm{RH})$. The extent to which δ may be regarded as an estimate of the same quantity for smaller primary n-alkyls may be seen by comparing entropies calculated by the complete method for ethyl and propyl with those calculated from the values of δ in Table 2 and the data of Rossini *et al.*[6] for ethane and propane. The approximate method yields values which are consistently higher than the complete calculations by, for ethyl, 0·75—0·62 e.u. and for propyl 0·32—0·25 e.u. These results lend credence to the view that our approximate method gives results for butyl and larger radicals which are entirely compatible with those calculated here for the smaller alkyls by the complete method. The results are, of course, subject to the same restrictions discussed for the complete calculations for small primary n-alkyls.

Results.—The results of the calculations are presented in Tables 1 and 2.

TABLE 1.

Direct calculations of radical entropies (cal. mole^{-1} deg.$^{-1}$) in the standard state, the ideal gas at 1 atm.

T (°K)	Methyl	Ethyl	Propyl	Isopropyl
200	42·86	54·84	63·34	61·10
298·16	46·43	59·22	69·32	67·55
300	46·48	59·29	69·42	67·66
400	49·31	63·14	74·97	73·33
500	51·71	66·70	80·21	78·55
600	53·80	70·04	85·19	83·45
700	55·69	73·15	89·80	88·02
800	57·42	76·11	94·20	92·38
900	58·99	78·92	98·38	96·50
1000	60·47	81·56	102·27	100·34

TABLE 2.

Calculations of the increment δ (cal. mole^{-1} deg.$^{-1}$) as a function of temperature.

T (°K)...	200	300	400	500	600	700	800	900	1000
δ.........	5·12	5·09	4·91	4·64	4·28	3·93	3·54	3·16	2·79

Limitations.—The accuracy of our calculations is determined principally by the validity of the rotational and vibrational models used, and is most readily assessed for the methyl radical. Here, the bond length is certainly known to better than ±1%, indicating a maximum uncertainty of ±0·06 e.u. in the rotational entropy. It seems unlikely that the estimates of the in-plane vibrational frequencies could be in error by more than 200 cm.$^{-1}$, which results *at most* in an uncertainty of ±0·37 e.u. in the vibrational entropy for the in-plane motions. The entropy associated with the out-of-plane vibration is subject to an uncertainty of a different kind. Herzberg's experimental results consist of a measurement of the energy difference between the ground state and the *second* excited state for this vibration. As Herzberg points out, this motion is likely to be markedly anharmonic. The experimental observations do not permit an estimate of the anharmonicity, but the *greatest* possible deviation from harmonicity would result from a square-well potential function for this co-ordinate. For such a function the eigenvalues are given by, $E = gn^2$, where g is a constant and n a running integer. The entropy associated with a square-well oscillator compatible with Herzberg's observations has been calculated by the direct-count method; the resulting values are found to be greater than the entropy for the harmonic model at temperatures below 600°K, and smaller above 600°K. At temperatures in the range considered here the entropies deduced for the two models do not differ by more than 0·34 e.u.; we therefore regard our calculations of the entropy for the out-of-plane vibration of methyl as being subject to an uncertainty not greater than 0·34 e.u.

Assuming that the uncertainties listed here are independent, and combining them accordingly we find that our values of S°_T for methyl are subject to an error of ±0·51 e.u.

For propyl the entropies calculated by the approximate and the detailed methods agree to ±0·3 e.u. It therefore seems likely that this figure represents the mutual consistency of the calculated entropies for all the radicals. Taken in conjunction with the estimated uncertainty in the calculated value of the entropy of methyl, this indicates that the calculations for the radicals other than methyl are good to within 1 e.u.

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[*Received, March* 16*th*, 1964.]