The Entropy of Acetone and Isopropyl Alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl Alcohol

S. C. Schumann and John G. Aston
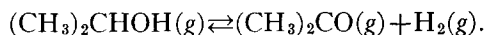
The Entropy of Acetone and Isopropyl Alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl Alcohol

S. C. Schumann and John G. Aston

School of Chemistry and Physics, The Pennsylvania State College, State College, Pa.

(Received June 8, 1938)

The entropy and free energy of acetone and isopropyl alcohol gases have been calculated from the molecular data at several temperatures on the basis of (a) free internal rotation (b) restricted rotation (with the potentials: Acetone, about $C-C$ bond $= 1000$ cal.; isopropyl alcohol, about $C-C$ bond $= 3400$ cal. about $C-O = 5000$ cal.). The va'ues based on restricted internal rotation were made to be consistent with the third law values. They are in better agreement with the ΔS values from the equilibrium data than those assuming free rotation.

I. INTRODUCTION

ANOTHER reaction which satisfies the conditions for detecting the presence of potentials hindering the rotation of groups in organic compounds[1-3] is the dehydrogenation of isopropyl alcohol to acetone

$$(CH_3)_2CHOH(g) \rightleftarrows (CH_3)_2CO(g) + H_2(g).$$

II. THE ENTROPY OF ACETONE AND ISOPROPYL FROM THERMAL DATA

Tables I and II summarize the calculation of the entropy of the hypothetically perfect gases at their normal boiling points.

III. THE ENTROPIES FROM MOLECULAR DATA

(a) Acetone

The assignment of frequencies to the twenty-two modes of vibration was made from the Raman data of Dadieu and Kohlrausch and of Trumpy.[10, 11]

Employing the principles of the previous paper[3] these are[12] $C-CO-C$ skeleton: $\nu_1(\pi)$, 780; $\nu_1(\sigma)$, 1070; $\nu_2(\pi)$, 1715; $\delta(\pi)$, 376; $\delta_1(\sigma)$, $= \delta_2(\sigma)$, 528. CH_3 (internal): $^2\nu(\pi)$, 2950; $^4\nu(\sigma)$, 2950; $^2\delta(\pi)$, 1220; $^4\delta(\sigma)$, 1432. $(CH_3)_2 > CO$ (hydrogen angle variation): $\delta_1 = \delta_2 = \delta_3 = \delta_4$, (880) (calc. free rotation): (950) (calc. restricted rotation). The average value of 880 cm^{-1} for last four frequencies δ_i which are similar to the $\nu_\alpha M$ frequencies in ethane was obtained from the gaseous heat capacity measurements,[13, 14] as discussed elsewhere[1, 15] on the assumption of free internal rotation. The value 950 cm^{-1} was obtained similarly on the basis of restricted rotation of methyl

TABLE I. *The calorimetric entropy of acetone at 329.3°K.*

	E.U./MOLE
0°K (cryst.)–298.16°K (liquid)[4]	47.9 ±.3
Liquid 298.16–329.3[5]	3.10 ±.05
Vaporization 7090/329.3[6]	21.53 ±.1
Entropy of actual gas at boiling point (329.3°K)	72.53 ±.5
Correction for gas imperfection[7]	.13
Entropy of ideal gas at boiling point	72.7 ±.5

TABLE II. *The calorimetric entropy of isopropyl alcohol at 355.5°K.*

	E.U./MOLE
0°K (cryst.)–298.16°K (liquid)[4]	43.0 ±.3
Liquid 298.16–355.5[8]	8.07 ±.2
Vaporization $\dfrac{(161.7 + 159.2)}{2 \times 355.5}$ 60.09[6, 9]	27.12 ±.2
Entropy of actual gas at boiling point (355.5°K)	78.19 ±.7
Correction for gas imperfection[7]	.09
Entropy of ideal gas at boiling point	78.3 ±.7

[1] Kemp and Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).

[2] Pitzer, J. Chem. Phys. **5**, 469, 473 (1937).

[3] Schumann and Aston, J. Chem. Phys. (See previous paper.)

[4] Kelley, J. Am. Chem. Soc. **51**, 1145 (1929).

[5] Williams and Daniels, J. Am. Chem. Soc. **47**, 1490 (1925).

[6] Matthews, J. Am. Chem. Soc. **48**, 562 (1926).

[7] From thermodynamics and the modified Berthelot equation—

Acetone	$P_c = 47$ atmos.	$T_c = 508$°K. I.C.T.
Isopropyl Alcohol	$P_c = 53$ atmos.	$T_c = 508$°K. I.C.T.

[8] Williams and Daniels, J. Am. Chem. Soc. **46**, 903 (1924).

[9] Parks and Nelson, J. Phys. Chem. **32**, 61 (1928).

[10] Dadieu and Kohlrausch, Monat **55**, 201 (1930).

[11] Trumpy, Kgl. Norske Videnskap Selskabs Skrifter No. 9, 1–20 (1935).

[12] $C-CO-C$ skeleton frequencies were assigned by comparison with formaldehyde. The ∂_2 frequency is predominantly CO stretching. The results of Duncan for the excited electronic states confirm this assignment. Duncan, J. Chem. Phys. **3**, 384 (1935).

[13] Wiedmann, Wied. Ann. **2**, 195 (1877).

[14] Regnault, Mem. de l'Acad. **26**, 1 (1862).

[15] See also Aston, Siller and Messerly, J. Am. Chem. Soc. **59**, 1743 (1937).

groups with the potentials found later. As will be evident presently, a method of successive approximations had to be used. The values obtained on the basis of restricted rotation are close to the average value for these vibrations in ethane (920 cm^{-1}). The vibrational entropy and free energy were calculated on the basis of these frequencies from Nernst's tables.

The rotational entropy and free energy were calculated on the basis of free rotation[3] using the distances: CH = 1.11A; CC = 1.54A CO = 1.24A[16] <CCC 109° 28′ (CCOC skeleton planar).

With the <CCC lying in the x, y plane, the y axis bisected this angle. The diagonal terms of the matrix of moment of inertia[17] using parallel axes through the center of gravity times 10^{40} are in order

$$83.9, \quad 90.6, \quad 174.5, \quad 5.46, \quad 5.46.$$

As the rest of the terms are zero these are reduced moments about the principal axes. The symmetry number is 18. The entropy and free energy due to rotation and translation are given, respectively, by

$$S_{t+r} = 10/2R \ln T + 11.545, \tag{1}$$

$$-((F - E_0')/T)_{t+r} = 10/2R \ln T + 1.611. \tag{2}$$

Table III (column 1) summarizes the calculations of the total entropy at the normal boiling

TABLE III. *The entropy of acetone from molecular data.*

	329.3°K FREE ROTATION	329.3°K RESTRICTED ROTATION
$S_{t,r}$	69.14	69.14
S_{vib}	4.15	3.99
$2(S_f - S)(CH_3, 1000 \text{ cal.})$	—	.48
Entropy of the ideal gas	73.29	72.65
Discrepancy	.6	—

point from molecular data on the basis of free rotation.

The discrepancy of 0.6 entropy units between this result and that from the thermal data (Table 1) is almost within the experimental error. However, a better fit can be obtained on the basis that a potential of 1000 calories re-

[16] Brockway, Rev. Mod. Phys. **8**, 231 (1936).

CH$_3$CHO; CO = 1.20A   Cl$_2$CO; CO = 1.28A.

[17] Kassel, J. Chem. Phys. **4**, 276 (1936).

TABLE IV. *The entropy of isopropyl alcohol from molecular data.*

	355.5°K FREE ROTATION	355.5°K RESTRICTED ROTATION
$S_{t,r}$	76.17	64.10
S_{vib}	6.35	6.15
$2S_{rr}(CH_3, 3400 \text{ cal.})$	—	4.96
$S_{rr}(OH, 5000 \text{ cal.})$	—	3.07
Entropy of the ideal gas	82.52	78.28
Discrepancy	4.2	—

stricts the internal rotation of each methyl group. Table III (column 2) summarizes the calculation on this basis. For such small potentials no great error has been found to result if the restricting terms are subtracted directly from the values for free rotation,[2] and this procedure has been followed for acetone.

(b) Isopropyl alcohol

The frequencies of isopropyl alcohol can be assigned by analogy with the spectra of ethyl alcohol and acetone. Using the Raman data of Dadieu, Pongratz, and Kohlrausch[18]

C−CO−C skeleton: $\nu_2(\pi)$, 815; $\nu_1(\pi)$, 875; $\nu_1(\sigma)$, 940; $\delta(\pi)$, 370; $\delta_1(\sigma)$, 420; $\delta_2(\sigma)$, 490.

CH$_3$ (internal): $^2\nu(\pi)$, 2870; $^4\nu(\sigma)$, 2920; $^2\delta(\pi)$, 1340; $^4\delta(\sigma)$, 1450.

OH (internal): ν, 3300.

CH (secondary) (internal): ν, 2900.

C−O−H (hydrogen angle variation): δ_7, (700).

(CH$_3$)$_2$>CH−O (hydrogen angle variation): $\delta_1 = \delta_2 = \delta_3 = \delta_4$, (880) (free rotation): (950) (restricted rotation); $\delta_5 = \delta_6$, 1105.

The frequencies $\delta_1 = \delta_2 = \delta_3 = \delta_4$ have been taken to be the same as the corresponding ones in acetone. δ_7 has been assigned the value for the analogous vibration in methyl alcohol. The assignment of 1105 cm^{-1} to $\delta_5 = \delta_6$ which are taken as due to angular motion of the CH group, is uncertain, but can produce no great error, as will be shown presently.

The rotational contributions were evaluated employing the same method and interatomic constants used previously for ethyl alcohol.[3] With axes along the same directions relative to the C−C−C grouping as were used for acetone,

[18] Dadieu, Pongratz, Kohlrausch, Monat. **61**, 369 (1932)

TABLE V.

$T°K$	FREE ROTATION ΔS	RESTRICTED ROTATION ΔS	ΔS EQUILIBRIUM DATA	
			C_p's F.R.	C_p's R.R.
355.5	24.69	28.28	—	—
400	25.08	28.39	—	—
450	25.41	28.44	27.89	27.37
500	25.61	28.35	28.26	27.52

the terms of Eq. (1) of the previous paper[3] times 10^{40} are:

$$(xx) = 88.69 - 1.95 \sin \alpha + 1.28 \sin^2 \alpha,$$
$$(yy) = 61.51 + 2.84 \cos \alpha + 0.86 \cos^2 \alpha,$$
$$(zz) = 34.85 - 2.21 \cos \alpha + 0.42 \cos^2 \alpha,$$
$$(xy) = 1.03 \sin \alpha + 1.05 \sin \alpha \cos \alpha,$$
$$(xz) = 1.46 \sin \alpha + 0.74 \sin \alpha \cos \alpha,$$
$$(yz) = -32.59 - 0.13 \cos \alpha + 0.60 \cos^2 \alpha.$$

(where α orients the OH group)

$$(\lambda\lambda) = 7.29, \quad (\mu\mu) = 4.07, \quad (\nu\nu) = 0.89,$$
$$(\lambda\mu) = 0, \quad (\lambda\nu) = 0, \quad (\mu\nu) = -0.63,$$
$$K_{OH} = 1.32, \quad K_{CH_3} = 5.46,$$
$$\sigma = 9.$$

The determinant is again a function of the angular position of the asymmetrical OH top. Assuming free rotation, the translational and rotational entropy and free energy are found to be:

$$S_{t+r} = 11/2R \ln T + 12.235 \tag{3}$$

$$-((F^0 - E_0^0)/T)_{t+r} = 11/2R \ln T + 1.307. \tag{4}$$

Table IV, column 1, summarizes the calculation of the entropy of isopropyl alcohol from the molecular data, assuming free rotation. The discrepancy from the thermal data of Table II can be explained by a potential of 3400 calories restricting the rotation of methyl groups and a barrier of 5000 calories hindering hydroxyl rotation. Table IV, column 2, summarizes the calculation at the normal boiling point using these potentials. In evaluating the rotational contributions for the rigid molecule, $[R_{\text{rigid}}]^{\frac{1}{2}}$ was averaged over all positions of the hydroxyl group. The calculation was thus similar to that for ethyl alcohol.[3] The symmetry number was taken to be unity for this part of the rotational entropy. In the calculation of the contribution of each hindered methyl group to the rotational
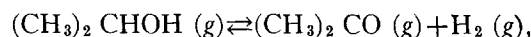
entropy, the symmetry number is, of course, three. Thus utilizing the above potentials, Eqs. (3) and (4) are replaced by (5) and (6)

$$S_{t+r} = 11/2 R \ln T + 12.020 - \sum(S_f - S), \tag{5}$$

$$-\left(\frac{F^0 - E_0^0}{T}\right)_{t+r} = 11/2 R \ln T$$
$$+ 1.092 - \sum\left(\frac{F - F_f}{T}\right). \tag{6}$$

IV. COMPARISON WITH THE EQUILIBRIUM DATA

Parks and Kelley[19] have obtained equilibrium data for the reaction,

$$(CH_3)_2 CHOH (g) \rightleftarrows (CH_3)_2 CO (g) + H_2 (g),$$

which are consistent to about 8 percent in K. The heat of this reaction has recently been measured at $355°K^{20}$ with an accuracy of 100 cal./mole. Table V summarizes the ΔS values, calculated from these data for the reaction as written above, and compares them with the values determined from molecular data both for free and restricted rotation, using the known entropy of hydrogen gas.[21, 22]

Column 2, Table V gives the results, at several temperatures, of the calculations from the molecular data, assuming free rotation. Column 3 lists results obtained on the basis of potential barriers, of the values determined above, re-

TABLE VI.

°K	RESTRICTED ROTATION ACETONE		RESTRICTED ROTATION ISOPROPYL ALCOHOL	
	S	$-\left(\frac{F^0 - E_0^0}{T}\right)$	S	$-\left(\frac{F^0 - E_0^0}{T}\right)$
355.5	74.15	60.08	78.29	62.73
400	76.73	61.77	81.61	64.68
450	79.58	63.55	85.23	66.78
500	82.23	65.28	88.71	68.81

stricting the rotation of methyl and hydroxyl groups. Column 4 lists values of ΔS calculated from the best straight line through the equilibrium data, using values of $\Delta H°$ extrapolated to

[19] Parks and Kelley, J. Phys. Chem. **32**, 734 (1928).
[20] We wish to thank Professor G. B. Kistiakowsky for giving us this result prior to publication. Dolliver, Gresham, Kistiakowsky, Smith, Vaughan, J. Am. Chem. Soc. **60**, 440 (1938).
[21] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[22] Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).

the desired temperature assuming free rotational heat capacities. The values in column 5 were calculated with $\Delta H°$ values extrapolated with the aid of heat capacities on the basis of restricted rotation. For completeness, the entropy and free energy of acetone and isopropyl alcohol is tabulated in Table VI from 355.5°K to 500°K on the basis of restricted rotation.

V. ACCURACY

The assignment of the δ_i frequencies in both acetone and isopropyl alcohol may cause an error of as much as 0.5 e.u. at 355°K and 0.8 e.u. at 500°K in the entropy of each compound. This error will largely cancel in the calculation of ΔS and in the extrapolation of ΔH. Neglecting the negligible error in the equilibrium constants themselves, the error in ΔS from the equilibrium measurements is that in ΔH_{355} plus that due to extrapolation. The total could hardly exceed 0.5 e.u. at 500°K.

The uncertainty in the calorimetric entropies of the gases is large. The comparison of the ΔS, based on restricting potentials determined calorimetrically, with that from the equilibrium data might be in error by as much as 2 e.u. at 500°K. Such an error is of course improbable. That the potentials solved for are of the expected order of magnitude is an indication of a much smaller error.

The comparison of the ΔS from the equilibrium data with that from the molecular data assuming free rotation could not be in error by more than 1 e.u. at 500°K and 0.7 e.u. at 355°K.

VI. DISCUSSION

It is apparent, in the case of isopropyl alcohol, that no assumption of error can explain the discrepancy of 4.2 e.u. between the third law entropy and that calculated assuming free rotation. Potential barriers hindering rotation, of the same order of magnitude found for other compounds, will account for the discrepancy. The high symmetry of the acetone molecule would suggest relatively free rotation about $C-C$ bonds: that the discrepancy in this case is only 0.6 e.u. tends to confirm this. No hypothesis based on random orientation in the crystal can square the results calculated on the basis of free rotation with those from the equilibrium measurements.

In view of the relatively high limit of error of these calculations, the check assuming restricted rotation is but a probable one. However the mass of accumulated evidence in favor of restricted rotation with potentials greater than 3000 calories[2, 3, 23, 24] leaves practically no doubt that this cause explains the lack of agreement of experimental third law entropies with these calculated on the basis of free rotation.

[23] Howard, J. Chem. Phys. **5**, 451 (1937).
[24] Kistiakowsky and Nazmi, J. Chem. Phys. **6**, 18 (1938).