throws serious doubt on the significance of a number of interpretations of interatomic distances in terms of bond types. It is evident that if interatomic distances are to be used as gages of bond order, tables of radii and methods of computation of separations to be expected for integral bond order must be clearly defined. These discrepancies indicate that this has not been done. I wish to argue that at the present stage of development of valence theory it is dubious whether this can be done.

Our prototype for a single covalent bond is H_2; the lower atomic weight dialkali molecules apparently contain such bonds. The r_e values for the hydrides of the alkali metals and of the halogens might be expected to follow a simple additivity relation were one to allow for the effect of electronegativity differences on the distribution of electrons in the region of the bond. But even there it does not appear possible to set up a completely self consistent scheme, (ref. 8, and Table II) for although the M–H distances in the hydrides of the first row elements are satisfactorily predicted, in SiH_4, PH_3, NaH and HI they are not. It follows that for molecules wherein the basic concept of bond of unit order is in itself fuzzy, wherein the extent of s–p hybridization to form orbitals of maximum stability is expected to change in going from one member of a series to another,[17] one can attach little significance to resonance schemes which purport to account for small deviations of the observed distances from those predicted on the basis of an inconsistent table of radii. The variety of factors which have been listed to date to account for deviations from additivity, such as effects of formal charge, incompleteness of valence shell, electronegativity differences, and the balance between the effect of nuclear charge on one atom as against the increase of electron density on the adjacent one,[7] etc., have in essence been attempts to "save" the notion that a chemical bond in a polyatomic molecule is indeed localized between two atoms. The advantages of such an approach are obvious; it is a good working hypothesis as long as some finer details are overlooked.

Acknowledgment.—The author wishes to express his sincere appreciations to the memory of the late Professor A. W. Browne for his interest in this structure determination and to the Trustee–Faculty Committee on Research of Cornell University for a grant supporting this investigation.

Summary

The diffraction of electrons by the vapor of difluorodiazine led to the following structure for that compound, based on the configuration F—N=N—F (*cis* and *trans*): N—F, 1.44 ± 0.04 Å.; N=N, 1.25 ± 0.04 A.; ∠NNF, 115 ± 5°. An attempt to determine the structure of fluorine azide was not successful.

The discrepancies between the interatomic distances observed and predicted for some fluorine compounds are reviewed, and it is suggested that the use of interatomic distances as a gage of bond orders be limited by discretion.

ITHACA, N. Y. RECEIVED DECEMBER 26, 1946

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[17] J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, I, sections 13, 20, 22, and 24 (1935).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE, STATE COLLEGE PENNSYLVANIA]

The Thermodynamics of Butadiene-1,2 from Calorimetric and Spectroscopic Data

BY J. G. ASTON AND G. J. SZASZ[1]

A study of the thermodynamic properties and a comparison of the experimental and calculated potential barriers for butadiene-1,2 (methylallene) and for ethylacetylene (1-butyne) is of interest primarily because they yield additional information about the potential function hindering internal rotation. In our earlier attempt to correlate and predict the magnitude of potential barriers,[2] it was found that a calculation based on hydrogen repulsions only, does not give satisfactory results for compounds containing an excess of electrons (*i.e.*, unsaturated compounds in general, dimethyl ether, dimethyl sulfide, etc.). Before extending the method so that it will yield correct results in such cases, it is desirable to have data on other compounds of this type. The present paper records the experimental data and potential barrier obtained for one of these compounds, butadiene-1,2.

The Calorimeter.—Figure 1 shows a diagram to scale, with explanatory legend of the apparatus used. The calorimeter itself is a modification of the one used by Aston and Eidinoff and is now desiguated as calorimeter B′. The surrounding system of shields, etc., has been modified to give better control of the temperature of all parts which may affect the calorimeter, and to make faster operation possible. The most important modification is the conical gold-plated copper cover over the glass cap of the resistance thermometer, which is attached to the calorimeter with Wood's metal and around which are wound the leads from the resistance thermometer and constantan heater. This is for the purpose of elimi-

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[1] Phillips Petroleum Fellow, 1945–1947.

[2] Aston, Isserow, Szasz and Kennedy, *J. Chem. Phys.*, **12**, 336 (1944).

[3] Aston and Eidinoff, THIS JOURNAL, **61**, 1533 (1939).

nating the effect of a temperature head in the leads which might otherwise produce errors in the heat input as calculated from the current and potential drop, due to conduction. It also eliminates the possibility of radiation from the glass cap if its temperature rises above that of the calorimeter due to temperature heads during energy input.

The constantan heater is connected in such a way as to avoid the necessity of making a lead correction in the heat input calculation. The heater potential was measured across the constantan heater and one of the identical current leads from the calorimeter to the shield in a manner used at the National Bureau of Standards.

The system outside the vacuum-tight container (7) is the same as used before. The filling tube is of stainless steel, one mm. i.d. two mm. o.d., closely wound with electrical heaters of B. and S. no. 30 (D.S.C.) constantan wires baked on with bakelite lacquer. These heaters have "tap-outs" of no. 36 copper wire, which also serve as thermocouples. The two lowest tap-outs can be seen at (14) and (16). Above (14) they are evenly spaced at 15-cm. intervals.

The heavy block of the old apparatus, (inside the container (7)) has been discarded and a "floating" ring is being used to bring all the electrical supply lead wires to the temperature of the calorimeter before reaching the side shield. All wires make two turns in this ring, which is wound with a no. 30 B. & S. constantan wire heater (50 ohms) and provided with a copper–constantan difference couple between itself and the side shield.

The Temperature Scale.—The strain-free platinum resistance thermometer, no. PT.S-3 was calibrated against laboratory standard thermocouple S-9.[4] The indications of the latter were checked by calibration against the hydrogen triple points and against hydrogen vapor pressures. The changes since the original comparison were as follows: $(T_{S-9} - T_{obs.})$ °K.; 0.10 at 13.96; 0.13 at 14.34; 0.22 at 15.81; 0.20 at 17.69; 0.17 at 19.31; 0.16 at 20.32. Above 90°K., it was possible to compare the laboratory temperature scale against the International Scale. The differences were as follows: ($T_{int.} - T_{lab.}$ in °K.): -0.06 at 90°K.; -0.05 at 150°K.; -0.01 at 200°K.; $+0.02$ at 250°K. Above 90°K. the International Temperature Scale, as established by calibrations at the oxygen, ice, steam and sulfur points, was used.

The Material.—The butadiene-1,2 sample used was obtained from the Phillips Petroleum Company. The original sample of about 95% purity was purified by fractionation through the new laboratory low-temperature fractionating column (about 30 theoretical plates). A middle portion of about 33 cc. at the boiling point was used as the calorimetric sample. This sample was freed of air by alternately warming nearly to the boiling point, cooling to liquid air temperatures and pumping off any vapor remaining over the sample. It was then introduced into the calorimeter in the customary manner.[5] This sample was found to contain about 0.11 mole per cent impurity as determined from equilibrium temperatures observed during melting and from premelting heat capacities.

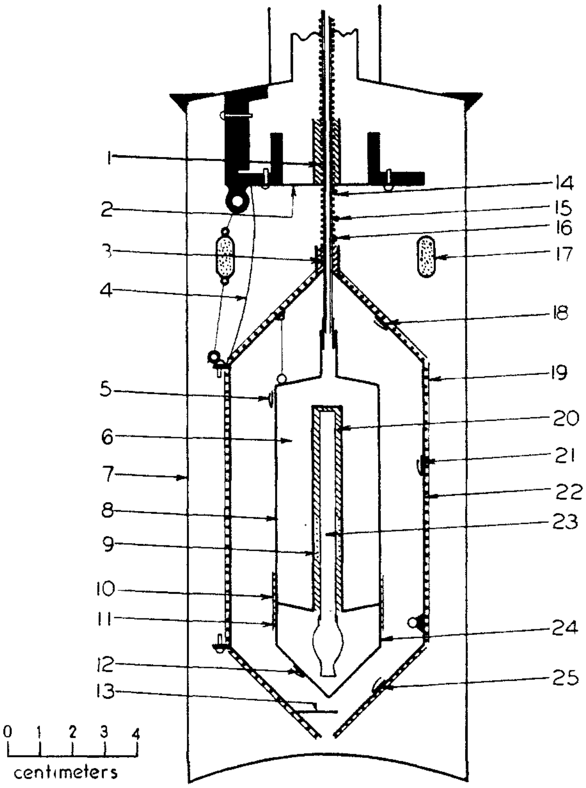

Fig. 1.—Calorimeter B': 1, paraffin filled ring; 2, copper strips from copper ring to provide cooling for filling tube; 3, Wood's metal filling; 4, thermal shunt of No. 18 B. & S. copper wire to provide cooling of shield at liquid hydrogen temperatures; 5, calorimeter vessel top difference thermocouple; 6, calorimeter vessel; 7, Monel cryostat can; 8, standard thermocouple; 9, Constantan heater; 10, electrical supply wires wrapped on heater shield; 11, Wood's metal contact; 12, calorimeter vessel bottom difference thermocouple; 13, evacuation hole radiation shield; 14, filling tube thermocouple No. 2; 15, filling tube shield top difference thermocouple; 16, filling tube thermocouple No. 1; 17, adiabatic ring; 18, shield top difference thermocouple; 19, adiabatic radiation shield heater; 20, Wood's metal filling; 21, shield side difference thermocouple; 22, adiabatic radiation shield; 23, platinum resistance thermometer; 24, heater radiation shield; 25, shield bottom difference thermocouple.

The Heat Capacity Measurements.—The method of measurement has been described before in papers dealing with adiabatic heat

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(4) Aston, Willihnganz and Messerly, THIS JOURNAL, **57**, 1642 (1935).

(5) (a) Aston and Messerly, *ibid.*, **58**, 2354 (1936); (b) Messerly and Aston, *ibid.*, **62**, 886 (1940).

capacity measurements.[3,6] Below the temperature region of appreciable vapor pressures, perfect temperature equality was maintained in all parts of the system. Under these conditions the temperature of the calorimeter did not show any drift (±0.0001° per minute) after reaching equilibrium. At the higher temperatures extreme precautions were taken to avoid any possibility of condensation in the filling tube. The shield top was offset by 0–0.1°, and the filling tube by 0.3–1.2°. These offsets produced warm drifts ranging from 0.0001–0.0005 deg. per minute, which were corrected for by extrapolation to the midtime of the heating period. Thus some of the advantage of the adiabatic calorimeter is lost. The electrical circuits used were essentially as described before.[5a,7] In most cases, the time of energy input for the heat capacities was measured by means of the laboratory automatic timer, which was checked against the Arlington time signals. In the remaining cases, the time was measured directly by a calibrated tenth second stop watch. One calorie was taken as equal to 4.1833 international joules.

The accuracy of the measurements is estimated to be ±0.1% between 30 and 200°K. Above this temperature the accuracy may drop to ±0.2% due to increasingly large vaporization correction. These corrections have already been discussed.[2] Below 30°K. the accuracy decreases due to the rapidly decreasing sensitivity of the resistance thermometer in this range.

Below 22°K. due to heat leak and attendant warm drift of the system, the heat capacities were not measured adiabatically. The indications of the resistance thermometer were followed at all times while the heating current was measured on a sensitive milliammeter which was calibrated using the White Double Potentiometer. The resistance of the constantan heater during heating was obtained in a separate series of measurements and the energy input was calculated from the current and resistance. Heating times ranged from thirty to ninety seconds, measured by a stop watch. The drifts were evaluated as calories/minute at the start and end of heating periods, and heat leak corrections made on this basis. The accuracy is estimated as ±1.0% at 20°K. and ±5% at 15°K.

Table I gives values for the heat capacities at rounded temperatures. These were obtained both from very sensitive plots and from analytical functions fitting the experimental data. Figure 2 shows the deviations of the experimental heat capacities from the values interpolated from Table I, at the same temperatures.

TABLE I

THE MOLAL HEAT CAPACITY OF BUTADIENE-1,2 AT ROUNDED TEMPERATURES

Mol. wt. 54.088; 0°C. = 273.16°K.; 1 cal. = 4.1833 in. joules.

Temp., °K.	C_p cal./deg./mole	Temp., °K.	C_p cal./deg./mole
	Crystal		Liquid
15	0.677	140	26.310
20	1.758	145	26.276
25	2.799	150	26.245
30	3.823	155	26.224
35	4.895	160	26.215
40	5.895	165	26.211
45	6.820	170	26.210
50	7.685	175	26.213
55	8.495	180	26.225
60	9.239	185	26.246
65	9.934	190	26.280
70	10.567	195	26.328
75	11.170	200	26.384
80	11.778	205	26.453
85	12.358	210	26.537
90	12.890	215	26.642
95	13.379	220	26.762
100	13.851	225	26.890
105	14.331	230	27.030
110	14.824	235	27.178
115	15.303	240	27.332
120	15.775	245	27.490
125	16.247	250	27.652
130	16.719	255	27.823
135	17.191	260	28.003
		265	28.198
		270	28.402
		275	28.619
		280	28.850
		285	29.093
		290	29.346

The Melting Point of Butadiene-1,2.—The equilibrium temperature of solid and liquid butadiene-1,2 was observed over a period of six hours with various fractions of the material melted as estimated from the heat input. From these results and the heat of fusion, the liquid soluble, solid insoluble impurity was found to be 0.11 mole per cent. Table II summarizes the data taken during melting. From these data the melting point of the pure material was calculated to be 136.95 ± 0.02°K. (−136.21°). The last column of this table gives equilibrium temperatures calculated from

$$\Delta T = \frac{RT^2}{\Delta H} N_2^0 \frac{100}{x} \qquad (1)$$

TABLE II

MELTING POINT OF BUTADIENE-1,2

0°C. = 273.16°K.

Melted, %	Total time, min.	T°K., obs.	T°K., calcd.
16	60	136.803	136.795
39	140	136.887	136.886
62	220	136.909	136.910
85	300	136.920	136.921
(100)	(Extrapolated)	136.925	136.925

Melting point of pure butadiene-1,2, 136.95 ± 0.02°K. (−136.21°). Mole per cent. impurity 0.11.

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[6] (a) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933); (b) Scott, Meyers, Rands, Brickwedde and Bekkedahl, *J. Res. Natl. Bur. Standards*, **35**, 39 (1945).

[7] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

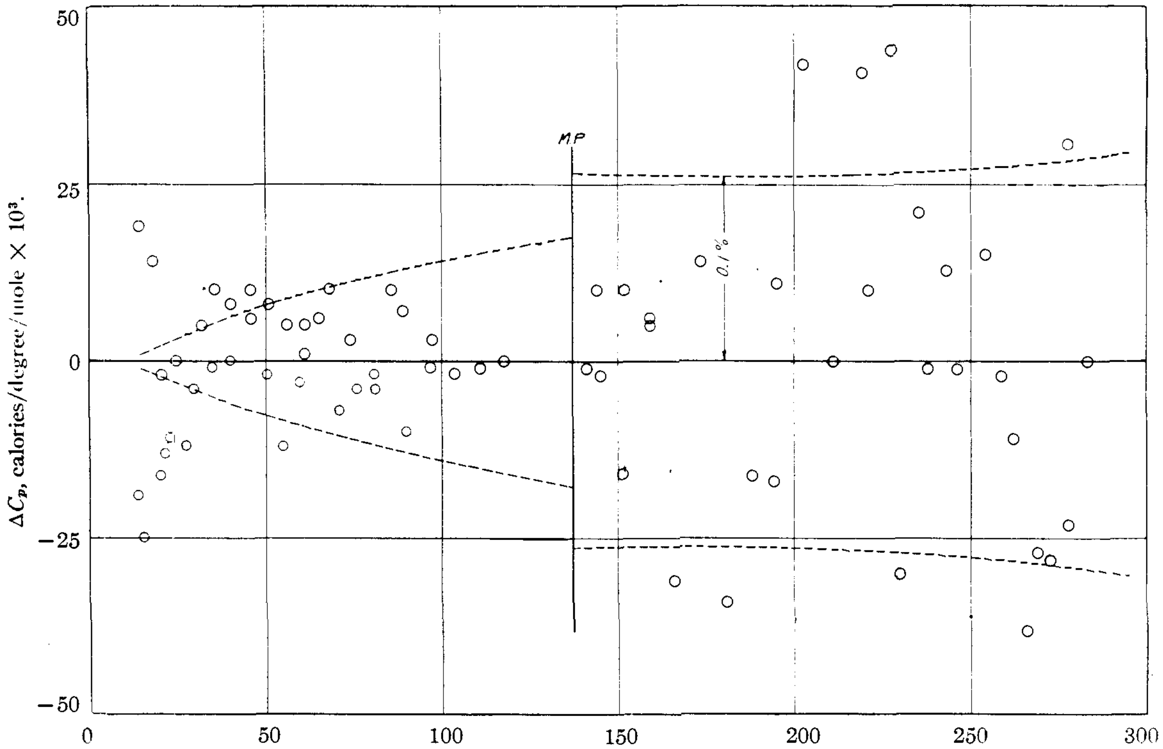

Fig. 2.—Deviation plot for butadiene-1,2: experimental points *vs.* smoothed curve.

where ΔT is the lowering from the melting point of the pure substance, ΔH is the heat of fusion, T is the melting point of the pure compound, N_2^0 is the mole fraction of the impurity in the completely melted sample and x is the per cent. melted when the lowering is ΔT.

The mole per cent. impurity calculated from the premelting heat capacity determinations[8] gave results ranging from 0.07% at 124.80°K. to 0.13% at 132.84°K.

The Vapor Pressures.—The results of the vapor pressure determinations, made as previously described,[4,5] are summarized in the equation

$$\log_{10} p_{\text{mm.}} = -(1413.58/T) + 1.48588 \log_{10} T - 0.00357508T + 5.23045 \quad (2)$$

This equation represents the experimental results between 200 and 280°K., obtained on the original sample, to within ±0.05 mm. However, the change in the vapor pressure when half the material has been removed from the calorimeter indicates the presence of some low boiling impurity and corresponds to about 0.14°K. change in the temperature. Distilling material until only $^1/_3$ remained produced no further effect indicating a poor choice of the fraction used for the sample for the vapor pressure measurements. This makes the pressures calculated from equation (2) uncertain to at least 0.14°K.; the equation is given in its precise form primarily as a means of obtaining precise values of dp/dt and the heats of vaporization from them. From equation (2) the normal boiling point is 283.86°K. (+10.70°). However, if it be assumed that the residue after distilling off two-thirds of the sample is pure material and a correction applied for the decrease in vapor pressure, the normal boiling point becomes 10.84°. This is the recommended value. Previous values reported were 10.3°[9] and 11.2–11.4° (780 mm.).[10] The last value becomes 10.5–10.7°, when corrected to 760 mm. using our pressure temperature coefficient.

The Heat of Fusion.—The data were taken along with the heat capacities in the usual manner.[5] The results are collected in Table III. The premelting correction was obtained by graphical integration between the corrected and uncorrected heat capacity curves below the starting temperature of the fusion.

TABLE III

HEAT OF FUSION OF BUTADIENE-1,2

Mol. wt. 54.088; 0.39305 mole in calorimeter; melting point, 136.925°K.

Temp., interval, °K.	Cor. heat input, cal./mole	$\int C_p dT$ cal./mole	Premelting cal./mole	ΔH fusion, cal./mole
134.491–138.705	1799.54	150.56	13.85	1662.83
131.131–140.082	1973.15	312.81	3.94	1664.28
130.004–140.807	2039.37	377.66	2.50	1664.20
			Average	1663.8 ± 1.0

The Heat of Vaporization.—Three heats of vaporization were taken at about 273°K. The

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(8) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(9) Hurd and Meinert, *ibid.*, **53**, 290 (1931).

(10) Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932).

method used was to adjust the rate of flow through a finely grooved stopcock to maintain a constant temperature and pressure during vaporization. This method has been described in detail in a previous communication.[11] The average temperature of the vaporization was estimated from the average pressures. The $\int C_p dt$ correction was obtained as follows: the temperature during vaporization (as measured by the pressure) was plotted against time and the net heat capacity of the system calculated at the midtime of intervals over which this curve was essentially linear. It was then only necessary to multiply each of these heat capacity values by the difference between the temperature at the midtime of the corresponding interval and the time-average temperature of vaporization and sum the results for the entire vaporization. The vaporization samples were weighed and thus the calorimeter contained very different amounts of material during the different measurements. The good agreement is an indication of equilibrium conditions and consistency in the correction terms. Table IV summarizes the data.

TABLE IV

MOLAL HEAT OF VAPORIZATION OF BUTADIENE-1,2 AT 273.25°K. AND 498.1 MM. PRESSURE

Moles vaporized	Mean temp. of vaporization, °K.	Total cor. heat input, cal.	$\int C_p dT$ cal.	ΔH at 273.25°K. to real gas state cal./mole
0.087155	273.22	515.587	−3.048	5880.5
.087366	273.29	513.664	+0.354	5883.1
.076640	273.26	454.545	−3.074	5890.9
			Average	5884.8 ± 6
Calculated from equation (2) and P_c = 42.6 atm., T_c = 449.3°K.[a] (Berthelot correction 160 cal.)				5873

[a] Critical constants were estimated using those of butadiene-1,3 and the relationship $(T_c/T_B)_1 = (T_c/T_B)_2$. For butadiene-1,3 $(T_c/T_B)_2 = 1.582$. P_c was taken as equal to that in butadiene-1,3.[6b]

TABLE V-a

THE MOLAL ENTROPY OF LIQUID BUTADIENE-1,2 AT 136.925°K.

Mol. wt. 54.088, 0°C. = 273.16°K.

	e. u.
0–13.5°K., Debye extrapolation (θ = 145.0, 5 degrees of freedom)	0.207 ± 0.020
13.5–136.925°K., $\int C_p/T\, dT$	16.750 ± .060
136.925°K., fusion (1663.8/136.925)	12.151 ± .005
Entropy of liquid at the melting point	29.108 ± .085 e. u.

TABLE V-b

THE MOLAL ENTROPY OF GASEOUS BUTADIENE-1,2 AT CERTAIN TEMPERATURES

Mol. wt. 54.088, 0°C. = 273.16°K.

T	230°K.		250°K.		273.25°K.		290°K.	
Liquid at melting point	29.108	± 0.085	29.108	± 0.085	29.108	± 0.085	29.108	± 0.085
136.925 − T, °K. $\int C_p d \ln T$	13.675	± 0.020	15.954	± 0.025	18.450	± 0.030	20.171	± 0.030
Vaporization at T, °K.	27.146[b]	± 0.200	24.397[b]	± 0.06	21.541[c]	± 0.020	19.541[b]	± 0.06
Gas imperfection cor.[a]	0.023		0.053		0.116		0.183	
Correction to 1 atm.	−5.075	± 0.010	−2.907	± 0.003	−0.824	± 0.002	+0.445	± 0.002
Entropy ideal gas at T, °K., 1 atm.	64.88	± 0.31	66.60	± 0.17	68.40	± 0.14	69.45	± 0.18

[a] $S_{\text{ideal}} - S_{\text{real}} = 27\,RT_c^3\,P/32\,T^3P_c$; P_c = 42.6 atm.; T_c = 449.3°K. [b] These values were calculated from the vapor pressure equation. [c] This is the measured value.

The Entropy from the Calorimetric Data.—The calculation for the liquid at the melting point is summarized in Table V-a while the calculations at 230, 250, 273.25 and 290°K. for the liquid, saturated vapor and ideal gas are given in Table V-b. The calculated values of the heats of vaporization may be in error due to the uncertainty in the vapor pressure equation.

The Spectroscopic Assignment for Butadiene-1,2.—The Raman spectrum of this compound has been determined by Bourguel and Piaux,[10] who investigated a series of substituted allenes. The infrared data have been obtained from American Petroleum Institute Spectrograms.[12] This molecule belongs to the symmetry class C_s and thus all fundamental frequencies should be both Raman and infrared active. The assignment chosen is as follows

	cm.$^{-1}$
C=C stretching	1071, 1961
C—C stretching	957
Skeleton angle change in plane	340, 420
Skeleton angle change out of plane	210
=CH_2 torsion	556
CH_3 internal angle change	1391, 1443, 1467
CH_2 internal angle change	1332
CH_3 wagging (rocking)	1002 1131
CH_2 wagging (rocking)	1182 1198
CH bending	886 1279
CH stretching	2870 2910 2954 2978 2993 3061

In making this assignment, the assiguments made for allene by Linnett and Avery,[13a] and for propylene by Wilson and Wells,[13b] and the assignment made for butene-1 by Aston, Szasz, Woolley and Brickwedde were considered.[14] The only line not found in the spectrum is the 420 cm.$^{-1}$ skeleton bending frequency. This leads to a bar-

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(11) Aston, Sagenkahn, Szasz, Moessen and Zuhr, THIS JOURNAL, **66**, 1175 (1944).

(12) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Infrared Spectrograms. Serial No. 41. Butadiene-1,2, contributed by the Shell Development Company, Emeryville, California.

(13a) Linnett and Avery, *J. Chem. Phys.*, **6**, 686 (1938).

(13b) Wilson and Wells, *ibid.*, **9**, 319 (1941).

(14) Aston, Szasz, Woolley and Brickwedde, *ibid.*, **14**, 67 (1946).

rier of 1650 cal./mole hindering the rotation of the methyl group. If instead of assiguing an unobserved frequency at 420 cm.$^{-1}$, the very weak Raman line at 525 be used for this vibration, a somewhat lower barrier of 1200 cal./mole is obtained. The results of this calculation are also summarized in Table VI. Considering the carbon skeleton frequencies of various C_4 hydrocarbons, a frequency of around 420 cm.$^{-1}$ seems reasonable; while the weak 525 cm.$^{-1}$ line seems somewhat high. The analogous frequencies in other compounds are listed in cm^{-1}: allene, 353; propylene, 417; propane, 333,375; methylacetylene, 336; butene-1, 320,437; butadiene-1,3, 362,513; cis-butene-2, 304,581; *trans*-butene-2, 290,507; dimethylacetylene, 213,374; *n*-butane, 326,250 and 428,185 for the two forms. Of the remaining lines a few weak ones may be due to impurity, but all can be accounted for as combination or overtone frequencies.

TABLE VI

THE ENTROPY OF BUTADIENE-1,2 IN THE IDEAL GAS STATE FROM MOLECULAR AND SPECTROSCOPIC DATA AT CERTAIN TEMPERATURES

T	230° K.	250° K.	273.27° K.	290° K.
Translation, external and internal rotation	62.945	63.691	64.486	65.018
Vibrational (420 cm.$^{-1}$ bending)	3.432	3.975	4.581	5.116
$-(S_f - S)$ V = 1650 cal./mole $I_{red} = 4.60 \times 10^{-40}$ g. cm.^{2}	−0.89	−0.81	−0.72	−0.67
Total	65.49	66.86	68.35	69.46
Vibrational (525 cm.$^{-1}$ bending)	3.205	3.725	4.309	4.829
$-(S_f - S)$ V = 1200 cal./mole $I_{red} = 4.60 \times 10^{-40}$ g. cm.^{2}	−0.57	−0.50	−0.44	−0.40
Total	65.58	66.92	68.36	69.45
Calorimetric	64.88	66.60	68.40	69.45

The Entropy from Spectroscopic and Molecular Data.—The atomic parameters used were: C=C, 1.34 Å., C—C, 1.54 Å., —C—H, 1.09 Å., =C—H, 1.06 Å., H—C—H angle 120° in $=CH_2$, tetrahedral for CH_3. The value obtained for the product of the principal reduced external moments of inertia was ABC = 1.131×10^{-114}(g.cm.^{2}),[3] while the reduced moment of the methyl group was found to be 4.598×10^{-40} g.cm.^{2} The symmetry number of the rigid molecule is 1 (class C_s). The entropy due to translation, external and free internal rotation of the methyl group $S_{t+r+int.\,rot.} = 20.5875 \log T + 14.324$. The comparisons between the calculated and experimental entropies are given in Table VI. The barrier chosen is 1650 cal./mole with a probable uncertainty of 300–400 cal./mole. As can be seen, the agreement at 230°K. is not as good as can be desired. This is perhaps due to the uncertainty in calculating the heat of vaporization from the vapor pressure equation. As an indication of possible limits of uncertainty, it is of interest to note that a barrier of 2300 cal./mole would bring the calculated entropy at 230°K. within 0.2 e.u. of the experimental value.

The Calculated Potential Barrier.—The potential barrier calculated by an empirical method,[2] based on hydrogen repulsions only, is 1000 cal./mole. It is of interest to note that in this method the effect of singlebonded neighboring carbon atoms, which were part of methyl groups, was implicitly included with the hydrogen interactions, tetramethylmethane being one of the substances used in adjusting the parameters. Thus, if other bonds (including double bonds) contribute, only for neighboring double bonded structures, *i.e.*, C=C, C=O, etc., do we have to add additional terms to the calculations.

As a first approximation we shall neglect the small differences caused by different bond lengths and different numbers of electrons, and take empirically 2500 cal./mole for this term. This will act in an opposite direction to the other repulsions since the symmetry has been displaced by 120/2 = 60 degrees. The barriers calculated by the old method were 1000 cal./mole for butadiene-1,2; 930 cal./mole for propylene and 1000 cal./mole for acetone. Using 2500 cal./mole for the double bonded structures, we get the following results by subtracting from it the above values.

Butadiene-1,2	calcd. 1500;	expt. 1650
Propylene	calcd. 1570;	expt. 2100
Acetone	calcd. 1500;	expt. 1400

The more rigorous application of this method will involve calculating the interactions of the electron pairs of the methyl groups with all other electron pairs, both in single bonded and double (or triple) bonded structures, all of them placed at the covalent radii from the nuclei. The excess electrons on the oxygen in acetone, dimethyl ether etc., must of course be located, which can be done by a consideration of the wave function. It is possible that this will lead to a generally applicable method of obtaining potential energy curves for molecules with hindered internal rotation.

Acknowledgments.—We wish to thank Mr. A. B. Bestul, who did a major part of the construction of the apparatus, and participated in the determination of the heat capacity of the empty calorimeter. Thanks are due Dr. H. L. Fink, Dr. J. A. Morrison and Dr. E. L. Pace for help with the experimental work. We thank Phillips Petroleum Company for making available the material. The work was carried out coöperatively with the Cryogenic Laboratory of the National Bureau of Standards and is part of a program on the thermodynamic properties of four-carbon hydrocarbons. Much of the apparatus was purchased with funds provided by the National Research Council. The work was made possible by the financial aid provided by the Phillips Petroleum Fellowship.

Summary

1. The heat capacities of butadiene-1,2 have been measured from 14 to 284°K.

2. The solid–liquid equilibrium temperature and the heat of fusion have been determined. The melting point is 136.95°K. (−136.21°).

3. The vapor pressures have been determined from 200 to 289°K. and the results represented by an equation leading to a value for the normal boiling point and to values of the heat of vaporization at 230, 250 and 290°K. The normal boiling point is 10.84°.

4. The heat of vaporization has been determined at 273.25°K.

5. An assignment of the fundamental frequencies has been made, and the comparison between the calculated and observed entropies yielded a value of 1650 ± 400 cal./mole for the potential barrier hindering the internal rotation of the methyl group.

State College, Pa. Received April 4, 1947

[Contribution from the Central Experiment Station, Bureau of Mines]

Studies of the Fischer–Tropsch Synthesis. II. Properties of Unreduced Cobalt Catalysts[1, 1a]

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Introduction

Most of the successful cobalt Fischer–Tropsch catalysts are prepared by precipitation with sodium or potassium carbonate from an aqueous solution containing cobaltous nitrate and promoters such as thoria, magnesia or copper as nitrates.[4,5] In some catalysts magnesia in the form of a fine powder in an aqueous slurry is added at the time of precipitation.[6] Kieselguhr as a catalyst support is usually added at the time of precipitation, but it has been reported that catalysts of equal activity and life can be prepared by the addition of the kieselguhr to the moist precipitate.[7] Surface area and pore volume studies of Fischer–Tropsch catalysts have not been reported, but Ries[8] has described these properties of catalysts which may be inferred to be somewhat similar to Fischer–Tropsch catalysts. The nitrogen isotherms at −195° of his catalysts were "S"-shaped but showed a definite hysteresis on desorption. Their surface areas were many times greater than that of the kieselguhr used as a support. These catalysts were usually evacuated for sixteen hours at 340° before the isotherms or pore volumes were determined, so that the metal was probably present as oxide.

In this paper, surface area and pore volume studies are reported for two types of unreduced cobalt Fischer–Tropsch catalysts, and for similar preparations with promoters, kieselguhr or both omitted. The properties of the catalysts are compared and related to properties of the kieselguhrs that they contain. Precipitated catalysts of the cobalt–thoria–kieselguhr (100:18:100) type are designated by the number 108, and catalysts of the cobalt–thoria–magnesia–kieselguhr (100:6:12:200), prepared with finely divided magnesia, are designated by 89. Properties of the kieselguhrs used in these catalysts have been described by Anderson, McCartney, Hall and Hofer.[9] In later papers surface area and pore volume data of reduced cobalt Fischer–Tropsch catalysts and catalyst testing data will be reported.

Experimental

The preparation of the 89-catalysts has been described previously.[1a] A catalyst similar to these was 112A, which had the same ratio of cobalt-thoria-magnesia-kieselguhr, of 100:6:8:200, and the magnesia was precipitated from magnesium nitrate and added to the solution of cobalt and thorium nitrates. Since magnesium carbonate is fairly soluble, 20% more magnesium nitrate than the calculated amount was used. The 89- and 112-types with magnesia, thoria, kieselguhr or all three omitted were prepared in an identical manner, except for the omission of one or more of these components. The 108-catalysts were prepared in a similar manner to the 89-catalysts, with the magnesia omitted and potassium carbonate used as a precipitant instead of sodium carbonate.

Recently, Hall[10] communicated to us that the compositions of the magnesia-containing catalysts were uncertain because of the high solubility of magnesium oxide and carbonate. Analyses of the catalysts confirmed this, the ratios of cobalt:thoria:magnesia in the following catalysts being: 89H, 100:7.6:11.4; 89V, 100:8.3:10.3; 89Z, 100:7.0:8.5; 89BB, 100:6.3:12.1; 89EE, 100:6.1:12.5; and 112A, 100:6.2:8.1. The data indicate that, in many cases, the percentage of magnesia was lower than anticipated. Variation in the amount of thoria may be due to variable amounts of water of hydration in the salts used in preparing the catalysts. In the 108-catalysts the ratios of cobalt to thoria were near to those anticipated: 108B, 100:19.0; and 108E, 100:17.5.

Catalysts of the 89-series and similar preparations without promoters, kieselguhrs, or both were prepared in 150 to 300-g. batches, except catalysts 89H, 89CC, and 89-EE, which were made in 6.8-kg. batches. All 108-type catalysts were made in 13.6-kg. batches.

The catalysts were studied in the form of granules (G),

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[1a] Part I of this series, Anderson, Krieg, Seligman and O'Neill, see text *Ind. Eng. Chem.*, **39**, 1548 (1947).

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[4] Fisher and Koch, *Brennstoff-Chem.*, **13**, 61 (1932).

[5] Annual Reports of Fuels Research Board for Years Ending March 31, 1937, p. 136; 1938, p. 186; 1939, p. 151.

[6] Hall and Smith, *J. Soc. Chem. Ind.*, **65**, 128 (1946).

[7] Private communication from C. C. Hall. This effect is also described in captured German documents.

[8] Ries, Van Nordstrand, Johnson and Bauermeister, This Journal, **67**, 1242 (1945).

[9] Anderson, McCartney, Hall and Hofer, submitted to *Ind. Eng. Chem.*, **39**, 1618 (1947).

[10] Private communication.