

$$K_2(P_\infty - P) - K_3(\text{BuF})[(P_\infty - P_0) - (P_\infty - P)] - K_4(\text{BuF}) = 0 \quad (10)$$

When the expression for (BuF) obtained from equation 10 is substituted in (9), the rate equation in terms of the experimental variables is

$$dP/dt = K_1(P_\infty - P) + \frac{K_2K_4(P_\infty - P)}{K_3[(P_\infty - P_0) - (P_\infty - P)] + K_4} \quad (11)$$

Upon integration of equation 11 and rearrangement of terms, equation 3 is obtained. If it is assumed that the contribution of reaction (4) to the total rate of reaction is negligibly small, equation 2 is obtained upon integration of equation 11 and rearrangement of terms. This would indicate that reactions (5) and (6) are the principal reactions in the mechanism, while reaction (4) becomes more important as the reaction is greatly accelerated, as, for example, in experiments 5, 6, 20-23 and 38. Since P_0 and the "steady state" concentration of catalyst are not accurately known, values of the rate constants in equation 11 cannot be calculated from the present data.

Mechanisms involving isobutylene, carbonium ions or free radicals as intermediates in reaction (5) cannot explain the initial kinetic effects in experiments 7, 8 and 35. In addition, mechanisms involving ions or free radicals involve too high an energy of activation, as shown by Pearson and Simons.⁵

The results of the present work indicate that a simple step by step mechanism cannot explain the experimental facts, but that a hydrogen or proton transfer is involved. This, despite the fact that the reaction under study is probably one of the very simplest of the organic chemical reactions of the condensation type, points out the necessity for a more critical examination of other reactions for which mechanisms have been proposed.

Acknowledgments.—We express our appreciation to the Allied Chemical and Dye Corporation for financial aid during part of the time this research was in progress. Thanks are due Dr. R. W. Taft, Jr., for his helpful suggestions concerning the interpretation of the data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXVI. Some Heat Capacity, Entropy and Free Energy Data for Seven Compounds Containing Oxygen

BY GEORGE S. PARKS, WILLIAM D. KENNEDY, ROBERT R. GATES, JOHN R. MOSLEY, GEORGE E. MOORE AND MELVIN L. RENQUIST

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Heat capacity measurements between 80 and 300°K. have been made upon the following seven compounds: *n*-heptyl alcohol, cetyl alcohol, furfuryl alcohol, cyclopentanol, *n*-butyraldehyde, *n*-heptaldehyde and methyl ethyl ketone. From these calorimetric data the corresponding molal entropies at 298.16°K. have been derived and in turn, with the aid of suitable enthalpy values, the free energies of formation have been computed for all the compounds, save the heptaldehyde.

The present measurements were made during the decade starting with 1940 and available facilities did not provide temperatures below the boiling point of liquid nitrogen. However, extrapolation of entropies below 80°K. introduces uncertainties of the order of one unit, or less, in the molal entropy of any of these compounds, corresponding to a maximum of about 300 cal. in the resulting free energy value. This latter figure is equivalent to an uncertainty of merely 0.012% in the heat of combustion of cetyl alcohol and about 0.049% in that of furfuryl alcohol. Thus the accuracy of the enthalpy data is generally the limiting factor in evaluating the molal free energies of such organic compounds.

Materials.—Our samples of these compounds were the best obtainable at the time of the measurements. The observed melting points and the mole % purity, as estimated from relative equilibrium melting temperatures in the course of fusion determinations, are given in Table I. In the case of the six substances which are liquids at room temperature the main impurities were undoubtedly the air (or nitrogen in the case of furfuryl alcohol) dissolved at 1 atm. pressure and small amounts of water. The values for the probable "weight % purity" given in the last column were accordingly computed on the assumption that these were the only significant contaminants.

The *n*-heptyl alcohol, *n*-butyraldehyde and *n*-heptaldehyde were Eastman Kodak Co. materials, which were dried,

TABLE I
OBSERVED MELTING POINTS AND ESTIMATED PURITY

Compound	Formula	M.p., °K.	Purity	
			Mole %	Wt. %
<i>n</i> -Heptyl alcohol	C ₇ H ₁₆ O	240.0	98.2	99.7
Cetyl alcohol	C ₁₆ H ₃₄ O	321.8	99.7	..
Furfuryl alcohol	C ₅ H ₆ O ₂	258.5	99.2	99.8
Cyclopentanol	C ₅ H ₁₀ O	256.9	99.8	99.9
<i>n</i> -Butyraldehyde	C ₄ H ₈ O	176.2	97.7	99.4
<i>n</i> -Heptaldehyde	C ₇ H ₁₄ O	229.3	96.9	99.5
Methyl ethyl ketone	C ₄ H ₈ O	186.0	99.7	99.9

respectively, with calcium oxide, calcium chloride and anhydrous sodium sulfate, and then fractionally distilled. The cetyl alcohol, also an Eastman Kodak Co. product, was used without further purification. The cyclopentanol and methyl ethyl ketone were special preparations which had been made for us by the Phillips Petroleum Co. and the Shell Development Co., respectively. The furfuryl alcohol was a similar preparation from the Quaker Oats Co., which we subsequently purified further in a fractional distillation over sodium carbonate in an atmosphere of nitrogen.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure

TABLE II
SPECIFIC HEATS (C_p) AT EVEN TEMPERATURES AND MEAN HEAT OF FUSION ($\Delta H_{fus.}$)^a
In calories per gram of substance; s = crystalline; l = liquid

T, °K.	n-Heptyl alcohol	Cetyl alcohol	Furfuryl alcohol	Cyclopentanol	n-Butyraldehyde	n-Heptaldehyde	Methyl ethyl ketone
80	0.167 s	0.147 s	0.152 s	0.187 s	0.162 s	0.213 s
90	.181	.162	0.135 s	.163	.204	.180	.229
100	.193	.176	.142	.176	.220	.196	.244
110	.205	.188	.149	.189	.236	.211	.257
120	.216	.199	.156	.204	.252	.224	.269
130	.227	.210	.163	.225	.269	.236	.281
140	.238	.221	.170	.249	.285	.249	.293
150	.248	.232	.178	.272	.302 s	.262	.304
160	.258	.243	.186	.288274	.316
170	.269	.254	.194	.285287	.328 s
180	.281	.264	.203	.293	.488 l	.300	.499 l
190	.293	.275	.212	.311	.488	.314	.499
200	.306	.286	.221488	.330	.500
210	.319 s	.297	.231	.348	.489	.360 s	.501
220309	.243	.358	.490502
230322	.255	.375	.491	.490 l	.504
240	.484 l	.336	.280 s	.382	.492	.492	.506
250	.492	.350396 s	.495	.494	.509
260	.504	.365	.457 l	.431 l	.500	.497	.513
270	.519	.383	.468	.449	.509	.502	.518
280	.535	.402	.478	.470	.522	.509	.524
290	.554	.435 s	.488	.492	.535	.517	.530
300	.577 l499 l	.515 l	.544 l	.526 l	.537 l
M.p.	240.4°	...	258.6°	257.4°	176.8°	229.8°	186.1°
$\Delta H_{fus.}$	37.38	...	31.99	4.26	36.81	49.37	28.12

^a In the calculation of these fusion values, the somewhat more rapid rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point. The observed melting points have also been corrected here for impurities in the samples.

have been fully described in other places.¹ In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained should ordinarily be less than 1.0%, except insofar as impurities in a sample may cause premelting at the upper temperatures of the crystals.² The fortuitous errors are usually under 0.25%.

Generally about forty specific heat determinations in the temperature interval between 78 and 300°K. were made on each substance. The results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read from this curve for various even temperatures. For the sake of spatial economy and ease of comparison these derived values, rather than the more numerous experimental ones, are recorded in Table II. They and also the mean fusion values are expressed in terms of the *defined* conventional calorie³ and with all weights reduced to a vacuum basis.

The crystalline cyclopentanol showed a sharp transition at 202.8°K. Two determinations of the heat of this transition yielded identical values of 10.29 cal. per gram, which was over twice the

magnitude of the heat of fusion. The specific heat curves for this substance also exhibited two small "humps" or maxima at about 162 and 237°K. The respective heat effects associated with these humps were only 0.19 and 0.30 cal./g.

Crystalline cetyl alcohol has an important transition at 307°K., and our specific heat measurements here indicate the approach to this change even at 290°. Parks and Rowe⁴ have estimated the magnitude of this heat of transition as 16.4 cal./g. as against a value of 34.9 cal./g. for the heat of fusion at 322.5°K.

Apparently a few specific heat measurements on n-heptaldehyde by Andrews⁵ provide us with the only earlier data for any of these compounds within the temperature range of our measurements. His results are inexplicably higher than ours by about 26% at 107° and 34% at 192°K. On the other hand, our value for furfuryl alcohol at 300° is about 2.0% above a curve obtained by a downward extrapolation of the recent measurements of Hough, Mason and Sage.⁶

Entropy Data.—Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.16°K. for these seven substances. The detailed data are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks

(1) G. S. Parks, *THIS JOURNAL*, **47**, 338 (1925); also G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(2) Recent heat capacity measurements at the National Bureau of Standards (D. C. Ginnings and G. T. Furukawa, *THIS JOURNAL*, **75**, 522 (1953)) on n-heptane and benzoic acid, two substances previously studied at Stanford, provide further support for this statement as to the accuracy of the results from our laboratory.

(3) The factor 0.23904 has been used in converting the international joule to this defined calorie.

(4) G. S. Parks and R. D. Rowe, *J. Chem. Phys.*, **14**, 507 (1946).

(5) D. H. Andrews, *J. Franklin Inst.*, **206**, 285 (1928).

(6) E. W. Hough, D. M. Mason and B. H. Sage, *THIS JOURNAL*, **73**, 1363 (1951).

TABLE III
ENTROPIES OF THE SUBSTANCES IN CALORIES PER DEGREE PER MOLE
s = crystalline; l = liquid

Substance	Mol. wt.	Crystals		Fusion	Liquid	S_{298}^0	$-\Delta S_f^0$ at 298.16°K.
		0-80°K.	Above 80°K.				
<i>n</i> -Heptyl alcohol (l)	116.205	15.55	31.27	18.07	13.00	77.9	205.82
Cetyl alcohol (s)	242.448	27.56	80.44			108.0	468.86
Cetyl alcohol (l)				37.0		145.0	431.86
Furfuryl alcohol (l)	98.103	11.71	21.12	12.13	6.64	51.6	97.84
Cyclopentanol (l)	86.135	11.66	30.36 ^a	1.43	5.89	49.3	138.06
<i>n</i> -Butyraldehyde (l)	72.108	10.50	14.67	15.01	18.81	59.0	95.79
<i>n</i> -Heptaldehyde (l)	114.189	13.55	30.27	24.53	14.93	83.3	169.21
Methyl ethyl ketone (l)	72.108	12.78	16.68	10.90	17.35	57.7	97.09

^a This value includes 4.37 e.u. for the entropy of transition in crystalline cyclopentanol at 202.8°K.

and Huffman⁷ for estimating the entropy increases from 0 to 80°K. The various increments from 80 to 298.16°K., which appear in the next three columns, were obtained by the usual methods directly from the experimental data. The results for the total entropy are then given in the second column from the right under the designation " S_{298}^0 "; they are probably reliable to within 1% in an absolute sense and to about half this figure for comparative purposes.

In the case of cetyl alcohol, which is the only crystalline substance at 298°K., we have utilized the fusion and transition data of Parks and Rowe⁴ to estimate the entropy change for the hypothetical fusion process at this temperature so as to be able to compare this alcohol with the other compounds in the liquid state.

The values of the entropies of formation (ΔS_f^0) given in the extreme right-hand column of Table III represent simply the differences between the S_{298}^0 for each substance and the corresponding values for the entropies contained therein. For this purpose we have used 31.211 e.u. for the entropy of $H_2(g)$, 1.361 e.u. for C (β -graphite) and 49.003 e.u. for $O_2(g)$.⁸

While it is the intention of the senior author to present elsewhere a review of entropy regularities among both hydrocarbons and representative organic compounds containing oxygen, a few significant features relating to these tabulated S_{298}^0 values may be briefly noted here. Thus our present data show an average increase of 7.46 e.u. per CH_2 increment in going from *n*-heptyl alcohol to the hypothetical liquid cetyl alcohol, which is in fairly good agreement with values of 7.90 e.u. reported by Parks and co-workers⁹ and 7.725 e.u. derived by Finke and others¹⁰ in their recent studies of the normal paraffin hydrocarbons. It is also interesting that the entropies of liquid *n*-heptyl alcohol and cyclopentanol are within 1% of the accepted values¹¹ for the parent hydrocarbons, *n*-heptane (78.52 e.u.) and cyclopentane

(7) K. K. Kelley, G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(8) D. D. Wagman, J. E. Kirkpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(9) G. S. Parks, G. E. Moore, M. L. Renquist, B. F. Naylor, L. A. McClaine, P. S. Fujii and J. A. Hatton, *THIS JOURNAL*, **71**, 3386 (1949).

(10) H. L. Finke, M. E. Gross, G. Waddington and H. M. Huffman, *ibid.*, **76**, 333 (1954).

(11) F. D. Rossini and co-workers, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Penna., 1953, pp. 468, 470.

(48.82 e.u.). Evidently the polar character of such liquid alcohols results in a tightening of intermolecular forces which roughly compensates for the intramolecular vibrational contribution of the hydroxyl group. On the other hand, *n*-heptaldehyde, in which polar characteristics are less pronounced, has a molal entropy 5.4 e.u. higher than the alcohol. Furthermore, we here observe that the entropy of methyl ethyl ketone is very close to that of the corresponding *n*-butyraldehyde, as might be expected in view of the common presence of a carbonyl group.

Free Energy Data.—We have also calculated the free energies of formation of these compounds (except *n*-heptaldehyde) by means of the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$. The results as well as the contributing enthalpy data are recorded in Table IV, where for comparative purposes we have included a free energy figure for *n*-butyl alcohol based on the entropy value of Parks, Kelley and Huffman.¹²

TABLE IV
ENTHALPIES AND FREE ENERGIES AT 298.16°K. IN KCAL./MOLE

Substance	ΔH_f^0	ΔF_f^0
<i>n</i> -Butyl alcohol (l)	-79.34	-40.13
<i>n</i> -Heptyl alcohol (l)	-97.22	-35.85
Cetyl alcohol (s)	-163.42	-23.62
Cetyl alcohol (l)	-151.73	-22.97
Furfuryl alcohol (l)	-66.03	-36.86
Cyclopentanol (l)	-71.74	-30.58
<i>n</i> -Butyraldehyde (l)	-58.94	-30.38
Methyl ethyl ketone (l)	-66.66	-37.71

The tabulated values for the enthalpies of formation (ΔH_f^0) of crystalline cetyl alcohol, furfuryl alcohol, cyclopentanol and methyl ethyl ketone have been taken from the table of Parks, Mosley and Peterson¹³ with a minor revision for the recent change in atomic weight of carbon.¹⁴ In turn, the value for the hypothetical liquid cetyl alcohol at 298°K. has been calculated from this result for the crystalline material with the aid of the theoretical fusion value ($\Delta H_{298} = 11.69$ kcal./mole) of Parks and Rowe.⁴ The enthalpy values for *n*-butyl alcohol and *n*-heptyl alcohol have been derived by

(12) G. S. Parks, K. K. Kelley and H. M. Huffman, *THIS JOURNAL*, **51**, 1969 (1929).

(13) G. S. Parks, J. R. Mosley and P. V. Peterson, Jr., *J. Chem. Phys.*, **18**, 152 (1950).

(14) E. Wichers, *THIS JOURNAL*, **76**, 2033 (1954). The heat of combustion of graphitic carbon becomes $\Delta H_{298}^0 = -94.0539$ kcal. with this new value.

revision of Rossini's "best" combustion values¹⁵ in terms of the presently accepted atomic weights and Jessup's corrected result¹⁶ for the heat of combustion of the benzoic acid standard. The value for *n*-butyraldehyde was then deduced from this butyl alcohol datum on the assumption that Kistiakowsky's result¹⁷ for the heat of dehydrogenation of ethyl alcohol to acetaldehyde can also be applied to the corresponding four-carbon compounds. In this latter case the heats of vaporization of the *n*-butyl alcohol and aldehyde were taken as 11.80 kcal.¹⁵ and 7.90 kcal.,¹⁸ respectively. Unfortunately, complete thermal data were not available for an analogous calculation in the case of *n*-heptaldehyde.

In general, the free energies so derived are probably reliable to within 0.08 kcal. per carbon atom,

(15) F. D. Rossini, *J. Research Natl. Bur. Standards*, **13**, 189 (1934).

(16) R. S. Jessup, *ibid.*, **36**, 421 (1946).

(17) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, *THIS JOURNAL*, **60**, 440 (1938).

(18) C. B. Longworth, an unpublished research in the Stanford Laboratory.

although in the case of *n*-butyraldehyde the error may possibly be twice this latter figure. While we shall not now resort to a detailed discussion of these results, it is noteworthy that the average change in molal free energy per CH₂ increment is here 1.43 kcal. in going from *n*-butyl alcohol to liquid cetyl alcohol as against a value of 1.21 kcal. previously found in the series of liquid normal paraffins.⁹ It is also interesting to observe the difference of 7.33 kcal. in the molal free energies of *n*-butyraldehyde and methyl ethyl ketone, which is certainly real although one might intuitively expect approximately equal free energies for such isomers. Likewise, a comparison of these values for the several alcohols with those for the parent hydrocarbons¹¹ demonstrates that the introduction of the hydroxyl group produces an average lowering of 35 kcal. in the molal free energy for the production of a primary alcohol as against about 39 kcal. in the formation of the secondary alcohol, cyclopentanol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Preparation and Properties of Trifluoroiodoethene¹

BY J. D. PARK, R. J. SEFFL² AND J. R. LACHER

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The preparation of perfluorovinyl iodide and its reaction with ethylene, vinyl fluoride, vinylidene fluoride, trifluoroethane 1,1-difluoro-2,2-dichloroethene and 1,1-difluoro-2-chloroethene is described and the structures of the resultant butenes are discussed. It has been found that the attacking perfluorovinyl free radical attaches itself to the variously substituted ethylenic carbon atoms in the order $\text{CH}_2 > \begin{matrix} \text{CFH} \\ \text{CHCl} \end{matrix} > \text{CF}_2 > \begin{matrix} \text{CCl}_2 \\ \text{CFI} \end{matrix}$. The preparation of some fluorinated butadienes is described.

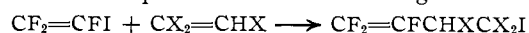
The new perfluorovinyl iodide has been synthesized from commercially available starting material. The first step in the synthesis involves the addition of hydrogen bromide to 1,1,2-trifluoro-2-chloroethene,³ dehalogenation to trifluoroethene followed by reaction with iodine monochloride to give 1,1,2-trifluoro-1-chloro-2-iodoethane (I). This result is in accord with the observation by Haszeldine⁴ that the negative substituent (in this case Cl⁻) becomes attached to the CF₂ group in the molecule.

CF₂=CFI (II) is prepared from I by treatment in a suspension of powdered potassium hydroxide in mineral oil. This particular medium was used rather than the traditional alcoholic potassium hydroxide since II reacts readily with alcoholic alkali to form ethers. The ultraviolet absorption spectrum of II shows a distinct band with the maximum at 258 mμ. This band is characteristic of aliphatic fluorinated iodides and Haszeldine⁵ re-

ports that the exact position of the band is dependent on the nature of the molecule.

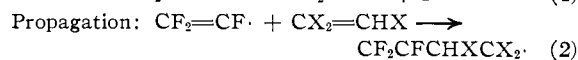
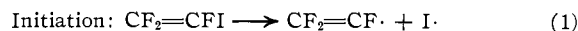
Free Radical Reactions of Perfluorovinyl Iodide—The Preparation of Some Fluorinated Butadienes

Perfluorovinyl iodide will react with other olefins such as ethylene, vinyl fluoride, vinylidene fluoride and trifluoroethene to form a linear 1:1 addition product in the presence of ultraviolet light as



where X = H or F.

In accordance with a general mechanism as proposed by Haszeldine,⁶ we propose the following mechanism for the reaction



It is to be noted that in step (1) the formation of a perfluorovinyl free radical is suggested. The existence of such a free radical has little precedent in the literature. With regard to other vinyl free radicals it is noted that Tickner and co-workers^{7a,b}

(6) R. N. Haszeldine, *ibid.*, 2856 (1949); **167**, 39 (1951); *Nature*, **165**, 152 (1950); *J. Chem. Soc.*, 3037 (1951).

(7) (a) A. W. Tickner, J. W. Hodgins and D. J. Leroy, *Can. J. Research*, **B26**, 619 (1948); (b) A. W. Tickner and D. J. Leroy, *J. Chem. Phys.*, **19**, 1247 (1951).

(1) Abstracted from a thesis by R. J. Seffl, submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1954. Presented before the Fluorine Subdivision of the Division of Industrial and Engineering Chemistry, 126th Meeting of the American Chemical Society, N. Y. C., Sept. 12-17, 1954.

(2) E. I. du Pont Predoctoral Fellow in Chemistry, 1953-1954.

(3) J. D. Park, W. R. Lycan and J. R. Lacher, *THIS JOURNAL*, **73**, 711 (1951).

(4) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

(5) R. N. Haszeldine, *ibid.*, 1764, 3761 (1953).