The most pronounced difference between the studies on the acids and on the thioacids lies in the temperature range. The present experiments were performed with $HBS_2(s)$ mostly at temperatures below 100°, where the principal species are $(HBS_2)_3(g)$ and $H_2S(g)$, but the experiments on the oxygen acids employed the reaction between water and boric oxide above 800°, where the principal species is $HBO_2(g)$. The great difference in the volatilities of the acids and thioacids arises presumably because of hydrogen bonding in the former.

The second difference is that the species found mass spectrometrically in the sulfur system are more numerous and more complicated than in the oxygen system.[4] The third difference is that metastable decompositions have not been reported for the oxygen acids. Finally, the extensive studies on the spectra and thermodynamic properties of oxygen species[4-6] have not yet been accomplished for the sulfur analogs.

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# Bond Energies and the Interactions between Next-Nearest Neighbors. III. Gaseous and Liquid Alkanes, Cyclohexane, Alkylcyclohexanes, and Decalins[1]

**A. Joseph Kalb,[2] Alice L. H. Chung, and Thomas L. Allen**

*Contribution from the Department of Chemistry, University of California, Davis, California 95616.* *Received January 20, 1966*

**Abstract:** The heats of formation of alkanes, cyclohexane, alkylcyclohexanes, and decalins are expressed as a linear function of seven structural parameters for both the gaseous and liquid states. Root-mean-square differences between calculated and experimental values are ±0.0185 kcal mole$^{-1}$ bond$^{-1}$ for 56 gases and ±0.0214 kcal mole$^{-1}$ bond$^{-1}$ for 63 liquids. In branched hydrocarbons the energy contributions by *gauche-n*-butane and *gauche–gauche* prime *n*-pentane structures are similar to those in the rotational isomers of normal paraffins. In some molecules the effect of a *gauche-n*-butane structure is accentuated by locking, where the H···H distance cannot be increased by internal rotation about any carbon–carbon bond without simultaneously decreasing the H···H distance in another interaction. The energetic effects of H···H interactions in ordinary and locked *gauche-n*-butane have been calculated independently by energy minimization.

In the first paper[3] of this series it was shown that inclusion of a single parameter, the next-nearest-neighbor interaction energy, removed practically all of the deviation from constancy in bond-energy calculations. Two other parameters, a trigonal interaction and a steric interaction between fifth-neighbor hydrogen atoms of the *gauche-n*-butane type, gave additional small but significant improvements. Molecules which were treated included the $C_1$ through $C_7$ alkanes, some cyclanes, diamond, the sulfanes, $S_8$, and some alkyl mercaptans, sulfides, and disulfides. This approach has been applied to many other molecules by McCullough and Good,[4] and by Skinner and co-workers,[5-10] and the theoretical basis of the method has been explored.[11,12]

The present study was undertaken to obtain more accurate equations for the heats of formation of saturated hydrocarbons and to obtain further information about steric interactions in these molecules. We were also interested in applying the method to liquids as well as gases.

## Treatment of Data

Our general approach was to adjust the coefficients in linear equations for heats of formation (similar to eq 33 and 35 of ref 3) so as to give optimum correlation with the experimental data. The equations were of the form

$$-\Delta H_f^\circ = A_K K + A_n n + A_X X + A_T T + A_S S + A_Z Z + A_L L \quad (1)$$

The $A$'s are the coefficients to be determined, and $K$, $n$, etc., are the structural parameters. $K$ reflects differences between the numbers of C–H and C–C bonds; it is 1 for acyclic, 0 for unicyclic, and −1 for bicyclic compounds. $n$ is the number of carbon atoms; $X$ is the number of pairs of next-nearest-neighbor carbon atoms. For the alkanes beyond methane it is conveniently calculated by eq 8 of ref 3. $T$ is the number of trigonal

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**Table I.** Comparison of Calculated and Experimental Heats of Formation

| Molecule[a] | $S$ | $Z$ | $L$ | $-\Delta H_f°$(exptl, 25°)[b] | | $\Delta H_f°$(calcd) − $\Delta H_f°$(exptl) | |
|---|---|---|---|---|---|---|---|
| | | | | Gas | Liquid | Gas | Liquid |
| −1 | 0 | 0 | 0 | 17.889 | ... | −0.01 | ... |
| −2 | 0 | 0 | 0 | 20.236 | 22.500[c] | 0.10 | −0.17 |
| −3 | 0 | 0 | 0 | 24.820 | 28.789[c] | −0.30 | −0.10 |
| −4 | 0 | 0 | 0 | 30.15 | 35.34[c] | 0.05 | 0.23 |
| 2m3 | 0 | 0 | 0 | 32.15 | 36.95[c] | 0.12 | 0.26 |
| −5 | 0 | 0 | 0 | 35.00 | 41.40[c] | −0.08 | 0.08 |
| 2m4 | 1 | 0 | 0 | 36.92 | 42.95[c] | 0.45 | 0.60 |
| 22m3 | 0 | 0 | 0 | 39.67 | 45.02[c] | −0.40 | −0.29 |
| −6 | 0 | 0 | 0 | 39.96 | 47.52 | −0.10 | −0.02 |
| 2m5 | 1 | 0 | 0 | 41.66 | 48.82 | 0.21 | 0.25 |
| 3m5 | 2 | 0 | 0 | 41.02 | 48.28 | 0.11 | 0.27 |
| 22m4 | 2 | 0 | 0 | 44.35 | 51.00 | 0.39 | 0.59 |
| 23m4 | 2 | 0 | 0 | 42.49 | 49.48 | −0.35 | −0.11 |
| −7 | 0 | 0 | 0 | 44.89 | 53.63 | −0.16 | −0.13 |
| 2m6 | 1 | 0 | 0 | 46.60[d] | 54.93 | 0.17 | 0.15 |
| 3m6 | 2 | 0 | 0 | 45.96[d] | 54.35 | 0.07 | 0.12 |
| 3e5 | 3[e] | 0 | 0 | 45.34 | 53.77 | 0.00 | 0.10 |
| 22m5 | 2 | 0 | 0 | 49.29 | 57.05 | 0.35 | 0.42 |
| 23m5 | 3 | 0 | 0 | 47.62 | 55.81 | 0.34 | 0.56 |
| 24m5 | 2 | 0 | 0 | 48.30 | 56.17 | 0.48 | 0.36 |
| 33m5 | 4 | 0 | 1 | 48.17 | 56.07 | 0.71 | 0.79 |
| 223m4 | 4 | 0 | 2 | 48.96 | 56.63 | −0.04 | 0.01 |
| −8 | 0 | 0 | 0 | 49.82 | 59.74 | −0.21 | −0.23 |
| 2m7 | 1 | 0 | 0 | 51.50 | 60.98 | 0.08 | −0.02 |
| 3m7 | 2 | 0 | 0 | 50.82 | 60.34 | −0.05 | −0.10 |
| 4m7 | 2 | 0 | 0 | 50.69 | 60.17 | −0.18 | −0.27 |
| 3e6 | 3 | 0 | 0 | 50.40 | 59.88 | 0.07 | −0.01 |
| 22m6 | 2 | 0 | 0 | 53.71 | 62.63 | −0.22 | −0.22 |
| 23m6 | 3 | 0 | 0 | 51.13 | 60.40 | −1.13 | −1.07 |
| 24m6 | 3 | 0 | 0 | 52.44 | 61.47 | 0.18 | 0.00 |
| 25m6 | 2 | 0 | 0 | 53.21 | 62.26 | 0.41 | 0.23 |
| 33m6 | 4 | 0 | 1 | 52.61 | 61.58 | 0.17 | 0.08 |
| 34m6 | 4 | 0 | 2 | 50.91 | 60.23 | −0.02 | −0.21 |
| 2m3e5 | 5 | 0 | 2 | 50.48 | 59.69 | 0.10 | −0.19 |
| 223m5 | 5 | 0 | 2 | 52.61 | 61.44 | −0.83 | −0.84 |
| 224m5 | 1 | 1 | 0 | 53.57 | 61.97 | (0.00)[f] | 0.57 |
| 233m5 | 6 | 0 | 2 | 51.73 | 60.63 | −1.17 | −1.10 |
| 234m5 | 5 | 0 | 2 | 51.97 | 60.98 | −0.35 | −0.48 |
| 3m3e5 | 6 | 0 | 4 | 51.38 | 60.46 | 1.20 | 0.80 |
| 2233m4 | 6 | 0 | 6 | 53.99 | ...[g] | −0.39 | ... |
| −9 | 0 | 0 | 0 | 54.74 | 65.84[h] | −0.27 | −0.35 |
| 33e5 | 8 | 0 | 8 | ... | 65.85[i] | ... | 2.04 |
| 2233m5 | 8 | 0 | 8 | ... | 66.54[i] | ... | −1.26 |
| 2234m5 | 4 | 1 | 2 | ... | 66.40[i] | ... | −0.65 |
| 2244m5 | 0 | 2 | 0 | ... | 66.95[i] | ... | −0.04 |
| 2334m5 | 8 | 0 | 8 | ... | 66.46[i] | ... | −0.52 |
| −10 | 0 | 0 | 0 | 59.67 | 71.95[h] | −0.32 | −0.46 |
| −11 | 0 | 0 | 0 | ... | 78.06[h] | ... | −0.57 |
| −12 | 0 | 0 | 0 | ... | 84.16[h] | ... | −0.68 |
| −16 | 0 | 0 | 0 | ... | 108.61[h] | ... | −1.10 |
| c6 | 0 | 0 | 0 | 29.43 | 37.34 | −0.46 | 0.04 |
| mc6 | 0 | 0 | 0 | 36.99 | 45.45 | 0.18 | 0.35 |
| ec6 | 1 | 0 | 0 | 41.05 | 50.72 | −0.20 | −0.04 |
| 11mc6 | 2 | 0 | 2 | 43.26[d] | 52.31 | 0.29 | 0.18 |
| *cis* 12mc6 | 3 | 0 | 2 | 41.15 | 50.64 | −0.15 | −0.11 |
| *trans* 12mc6 | 1 | 0 | 0 | 43.02 | 52.19 | −0.16 | −0.16 |
| *cis* 13mc6 | 0 | 0 | 0 | 44.16 | 53.30 | 0.44 | 0.40 |
| *trans* 13mc6 | 2 | 0 | 2 | 42.20 | 51.57 | 0.35 | 0.26 |
| *cis* 14mc6 | 2 | 0 | 2 | 42.22 | 51.55 | 0.37 | 0.24 |
| *trans* 14mc6 | 0 | 0 | 0 | 44.12 | 53.18 | 0.40 | 0.28 |
| pc6 | 1 | 0 | 0 | 46.20 | 56.98 | −0.03 | 0.00 |
| bc6 | 1 | 0 | 0 | 50.95 | 62.91 | −0.26 | −0.29 |
| dc6 | 1 | 0 | 0 | ... | 100.04[j] | ... | −0.46 |
| *trans*-Decalin | 0 | 0 | 0 | 43.57[k] | 55.14[k] | 0.05 | 0.04 |
| *cis*-Decalin | 3 | 0 | 3 | 40.38[k] | 52.45[k] | −0.33 | −0.26 |
| Av difference | | | | | | ±0.29 | ±0.36 |

[a] The symbolic nomenclature is adapted from J. R. Platt, *J. Phys. Chem.*, **56**, 328 (1952). The last digit is the longest carbon chain, m is methyl, e is ethyl, p is *n*-propyl, b is *n*-butyl, d is *n*-decyl, and c6 is cyclohexane. For example, 223m4 is 2,2,3-trimethylbutane, 2m3e5 is 2-methyl-3-ethylpentane, and 11mc6 is 1,1-dimethylcyclohexane. [b] All values in kcal mole$^{-1}$. Except as noted, experimental data are from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p tables. [c] "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Chemical Thermodynamic Properties Center, Texas A and M University, College Station, Texas, April 30, 1955, Table 1p. [d] The heats of vaporization of these substances are based on the experimental vapor pressure data of A. F. Forziati, W. R. Norris, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 555 (1949), together with the required auxiliary values for the compressibility factor and change in heat content with pressure for the gas and the molal volume of the liquid evaluated from data for analogous substances (F. D. Rossini, private communication). [e] Erroneously listed as 4 in ref 3. [f] As this is the only gaseous substance with $Z \neq 0$ in this study, the difference vanishes automatically. [g] The heat of formation listed in ref *b* should refer to the solid. [h] Reference *c*, October 31, 1954, Table 20p (part 1). [i] A. Labbauf, J. B. Greenshields, and F. D. Rossini, *J. Chem. Eng. Data*, **6**, 261 (1961). [j] Based on the heat of combustion determined by M. C. Loeffler and F. D. Rossini, *J. Phys. Chem.*, **64**, 1530 (1960). [k] T. Miyazawa and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 60 (1958).

interactions (sets of three carbon atoms bonded to a fourth carbon). If $C_3$ and $C_4$ are the numbers of tertiary and quaternary carbon atoms, respectively, then

$$T = C_3 + 4C_4 \qquad (2)$$

$S$ is the minimum number of fifth-neighbor H···H interactions of the *gauche-n*-butane type.

The last two parameters, $Z$ and $L$, were not considered in part I. It has been known for some time that certain alkanes (starting with 2,2,4-trimethylpentane) exhibit severe crowding and high steric strain energies.[5,6,13–17] Molecular models with a staggered configuration about each C–C bond show steric interactions of the *gauche–gauche* prime *n*-pentane type,[13,18–21] in which sixth-neighbor hydrogen atoms are forced into close proximity. $Z$ is the minimum number of interactions of this type. Finally, $L$ is the minimum number of $S$-type interactions which are locked; that is, the H···H distance cannot be increased by internal rotation about any C–C bond without simultaneously decreasing the H···H distance in another $S$-type or a $Z$-type interaction. Locking blocks the twisting release mechanism, leading to a higher steric repulsion energy.[5,6] It may be seen most clearly in 2,2,3,3-tetramethylbutane, where locking is exhibited by all six of the S-type interactions.

As this treatment of steric interactions applies only to molecules which nominally have staggered rotational configurations, the correlation has been restricted to acyclic molecules and cyclic molecules with six-membered rings. Table I lists all of the molecules

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**Table II.** Optimum Coefficients

| | 7-Parameter eq | | 6-Parameter eq | |
|---|---|---|---|---|
| | Gas | Liquid | Gas | Liquid |
| $A_K$[a] | 15.660 ± 0.157 | 14.930 ± 0.728 | 15.599 ± 0.191 | 15.799 ± 0.743 |
| $A_n$ | 2.237 ± 0.097 | 3.871 ± 0.356 | 2.323 ± 0.118 | 3.485 ± 0.368 |
| $A_X$ | 2.745 ± 0.096 | 2.346 ± 0.345 | 2.673 ± 0.117 | 2.727 ± 0.355 |
| $A_T$ | −0.811 ± 0.081 | −0.762 ± 0.257 | −0.819 ± 0.099 | −1.051 ± 0.264 |
| $A_S$ | −0.545 ± 0.054 | −0.557 ± 0.069 | −0.687 ± 0.056 | −0.722 ± 0.053 |
| $A_Z$ | −2.836 ± 0.500 | −3.592 ± 0.308 | −2.552 ± 0.609 | −3.612 ± 0.335 |
| $A_L$ | −0.392 ± 0.077 | −0.240 ± 0.070 | ... | ... |
| Rms deviation[b] | ± 0.0185 | ± 0.0214 | ± 0.0227 | ± 0.0233 |

[a] All coefficients in kcal mole$^{-1}$. [b] In kcal mole$^{-1}$ bond$^{-1}$.

of these types for which accurate experimental heats of formation are available, their *S*, *Z*, and *L* parameters (determined by examining molecular models for various conformations), and the experimental data for standard heats of formation in the gaseous and liquid states at 25°. Where the heats of combustion or vaporization are based on other correlation methods, the corresponding heats of formation have been excluded from this study.

The optimum coefficients were determined on an IBM 7044 computer at the Computer Center, University of California, Davis, using a linear regression program with a least-squares criterion. The total number of covalent bonds in each molecule, N, was applied as an inverse weighting factor to prevent the larger errors in the experimental data for the more complex molecules from unduly influencing the least-squares fit.

$$-\Delta H_f°/N = A_K(K/N) + A_n(n/N) + A_X(X/N) + A_T(T/N) + A_S(S/N) + A_Z(Z/N) + A_L(L/N) \quad (3)$$

The program generated the $-\Delta H_f°/N$ vector and the $K/N$, etc., matrix from the heats of formation and structural parameters of each molecule. By suppressing the locking parameter, six-parameter equations were also obtained. Table II lists the optimum coefficients and their standard errors, and the root-mean-square deviation of each correlation. Including the locking parameter reduces the rms deviation by 18% for the gases and 8% for the liquids. As the heats of combustion on which the heats of formation are based are all about 52 to 53 kcal mole$^{-1}$ bond$^{-1}$, the rms deviations listed in Table II correspond to differences of about ±0.04% between calculated and experimental data. Individual differences between experimental results and results calculated from the seven-parameter equations are shown in Table I.

The experimental heats of formation listed in Table III are probably less accurate than those of Table I because the samples were not of such high purity, and therefore these data were not used in determining the optimum coefficients. Calculated values are listed for comparison, together with root-mean-square differences between calculated and experimental data.

**Table III.** Further Comparison of Calculated and Experimental Data

| | | | | $-\Delta H_f°$ (liquid, 25°)[a] | | |
|---|---|---|---|---|---|---|
| Molecule | *S* | *Z* | *L* | Calcd (6 parameters) | Calcd (7 parameters) | Exptl |
| 3355m7 | 4 | 2 | 2 | 76.5 | 76.7 | 77.9[e] |
| 22445m6 | 4 | 2 | 2 | 78.2 | 78.3 | 78.7[e] |
| 2255m7 | 6 | 0 | 1 | 82.3 | 83.0 | 84.0[e] |
| 35m35e7 | 8 | 2 | 4 | 86.1 | 86.4 | 86.2[e] |
| 3366m8 | 8 | 0 | 2 | 87.1 | 87.9 | 89.1[e] |
| 4466m9 | 4 | 2 | 2 | 88.9 | 89.1 | 88.7[e] |
| 46m46e9 | 8 | 2 | 4 | 98.5 | 98.9 | 99.2[e] |
| 5577m11 | 4 | 2 | 2 | 101.4 | 101.6 | 103.7[e] |
| 3c6-20 | 5 | 0 | 3 | 161.3 | 161.3 | 159.6[f] |
| 9c6-20 | 5 | 0 | 3 | 161.3 | 161.3 | 161.5[f] |
| 11,c6-21[b] | 5 | 0 | 3 | 167.5 | 167.5 | 165.07[g]<br>165.3[f] |
| 5b22 | 3 | 0 | 0 | 171.4 | 171.8 | 171.0[f] |
| 11,b22[b] | 3 | 0 | 0 | 171.4 | 171.8 | 171.5[f] |
| 13,c6-25[c] | 5 | 0 | 3 | 192.3 | 192.4 | 189.92[g] |
| 11,d21[b] | 3 | 0 | 0 | 202.4 | 202.9 | 201.72[g]<br>204.4[f] |
| Rms deviation[d] | | | | ±0.0282 | ±0.0230 | |

[a] All values in kcal mole$^{-1}$. [b] First two digits represent eleven. [c] First two digits represent thirteen. [d] In kcal mole$^{-1}$ bond$^{-1}$. [e] Reference 17. [f] J. W. Knowlton and H. M. Huffman, *J. Am. Chem. Soc.*, **66**, 1492 (1944). [g] G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii, and L. A. McClaine, *ibid.*, **68**, 2524 (1946).

## Discussion

It would be of interest to know to what extent the deviations listed in Table I are caused by experimental errors and to what extent they represent inadequacies in the equations. Most of the differences appear to be well within the uncertainty intervals of the experimental data, but a few are rather large. It is surprising that the correlation works as well for liquids as for gases. For the 53 molecules where we have experimental data for both states (excluding 224m5), the average difference is 0.29 for gases and 0.28 kcal mole$^{-1}$ for liquids. We have attempted, without success, to discern some pattern in the deviations which would lead to a few additional useful parameters. Of course, the experimental data can be reproduced to any desired accuracy by adding enough parameters, but the correlation then loses its significance.

A likely source of small errors in the calculated values is the use of parameters based on the conformation of lowest energy, whereas at 25° most of these molecules are distributed among different rotational isomers. For the gases this can be avoided by using experimental data for 0°K, but the necessary heat capacity data are lacking for many of the larger molecules. For the smaller molecules, it is shown in part I that the general features of the correlation are the same whether one uses data for 25°, 0°K, or 0°K corrected for zero-point energies.[3] Therefore it appears that for data at 25° the major effects of rotational isomerism are absorbed by the coefficients. A more detailed approach would be to calculate the enthalpies, entropies, and equilibrium concentrations of all conformations, and thus obtain the average enthalpy.

The strain, $A_S$, associated with the *gauche-n*-butane conformation apparently arises from the mutual repulsion of a pair of hydrogen atoms, one in each methyl group.[18,22] We have calculated a theoretical value of 0.76 kcal mole$^{-1}$ for $A_S$ on the assumption that a minimum-energy configuration is attained by small torsions about C–C bonds and slight bending of bond angles, increasing the nonbonded H···H distance. (Details of the calculation are given in the Appendix.) The result agrees fairly well with our empirical values of 0.55 ± 0.05 kcal mole$^{-1}$ (gas data) and 0.56 ± 0.07 kcal mole$^{-1}$ (liquid data), and with values of 0.5 to 0.8 kcal mole$^{-1}$ for normal paraffins.[18,23–25] We find that the minimum value for $A_S$ is attained at torsional increments of approximately 2° about the central C–C bond and 6.5° about the end C–C bonds, and at increments in bond angles of about 1°. These results are not inconsistent with structural measurements.[25,26] If the structure is locked in the regular staggered configuration, angular distortions increase by about two-thirds and the strain energy increases by 0.28 kcal mole$^{-1}$, an amount not greatly different from the empirical values for $A_L$ of 0.39 ± 0.08 kcal mole$^{-1}$ (gas data) and 0.24 ± 0.07 kcal mole$^{-1}$ (liquid data).

In the $C_8$ alkylcyclohexanes listed in Table I there are three ordinary and eight locked *gauche-n*-butane interactions. The values of $A_S$ and $A_L$ in Table II for gases lead to an average steric interaction energy of 0.83 kcal mole$^{-1}$. A value of 0.9 kcal mole$^{-1}$ was obtained from heat capacity data for these molecules.[27]

The results for $A_Z$ (2.8 ± 0.5 for gases, 3.6 ± 0.3 for liquids) are in fairly good agreement with the values of 2.56 and 2.28 kcal mole$^{-1}$ obtained from intrinsic viscosity measurements on polyethylene.[20]

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## Appendix

The higher energy of *n*-butane in the *gauche* form relative to that of the *trans* rotational isomer may be regarded as arising from three sources: (a) mutual repulsion of a pair of nonbonded hydrogen atoms, one in each methyl group; (b) torsional strain due to deviations from a strictly staggered configuration; and (c) bending strain due to deviations of bond angles from their equilibrium values in the *trans* form.

To evaluate the first term we use the repulsive part of Bartell's potential function for nonbonded hydrogen atoms[28]

$$E(\text{repulsion}) = k_r \exp(-r/0.245) \qquad (4)$$

where $k_r$ is 4.58 × 10$^{-10}$ erg and $r$ is in A. Although the London energy term is dropped mainly to simplify the calculation, there is some evidence suggesting that it is better to use only the repulsive part of the potential at the distances involved in this calculation.[29,30]

The second term is obtained from $V(\theta) = V_0(1 - \cos 3\theta)/2$, where $\theta$ is the increment in the torsional angle with respect to the regular staggered configuration.[31] For small $\theta$, this may be approximated by $V(\theta) = 9V_0\theta^2/4 = {}^1/_2k_\theta\theta^2$. Assuming 2.875 ± 0.125 kcal mole$^{-1}$ for $V_0$ as in ethane,[31] we obtain 0.90 × 10$^{-12}$ erg radian$^{-2}$ for $k_\theta$. If $\theta_1$ refers to the central carbon–carbon bond and $\theta_2$ refers to either of the end carbon–carbon bonds, then

$$E(\text{torsion}) = k_\theta({}^1/_2\theta_1^2 + \theta_2^2) \qquad (5)$$

For the third term we consider only the bond angles which directly affect the distance $r$, namely, one CCH angle in each methyl group and the two CCC angles. If $\alpha$ and $\beta$ are the deviations of the CCC and CCH angles, respectively, from their equilibrium values in *trans-n*-butane, then

$$E(\text{bending}) = 2({}^1/_2k_\alpha\alpha^2 + {}^1/_2k_\beta\beta^2) = k_\alpha\alpha^2 + k_\beta\beta^2 \qquad (6)$$

The bending force constants $k_\alpha$ and $k_\beta$ are taken as 10.84 × 10$^{-12}$ and 6.50 × 10$^{-12}$ erg radian$^{-2}$, respectively.[32]

The nonbonded distance, $r$, is approximated by the expression

$$r = r_0 + T_1\theta_1 + T_2\theta_2 + A\alpha + B\beta \qquad (7)$$

which fits rather well for small angles. Applying the bond angles and bond distances of *trans-n*-butane as determined by Bonham and Bartell[26] to the *gauche* conformation in a regular staggered configuration, we calculate 2.08 A for $r_0$. For small deviations from this structure, $T_1$ is 0.23, $T_2$ is 1.42, $A$ is 2.64, and $B$ is 1.46 A radian$^{-1}$.

To obtain the equilibrium configuration, we minimize the total energy and obtain a set of simultaneous equations.

$$\frac{\partial E(\text{total})}{\partial \theta_1} = k_\theta\theta_1 - \frac{k_r}{0.245}\exp(-r/0.245)\frac{\partial r}{\partial \theta_1} = 0 \qquad (8)$$

$$\frac{\partial E(\text{total})}{\partial \theta_2} = 2k_\theta\theta_2 - \frac{k_r}{0.245}\exp(-r/0.245)\frac{\partial r}{\partial \theta_2} = 0 \qquad (9)$$

$$\frac{\partial E(\text{total})}{\partial \alpha} = 2k_\alpha\alpha - \frac{k_r}{0.245}\exp(-r/0.245)\frac{\partial r}{\partial \alpha} = 0 \qquad (10)$$

$$\frac{\partial E(\text{total})}{\partial \beta} = 2k_\beta\beta - \frac{k_r}{0.245}\exp(-r/0.245)\frac{\partial r}{\partial \beta} = 0 \qquad (11)$$

Also, we have $\partial r/\partial \theta_1 = T_1$, etc. Solution of these equations gives $\theta_1 = 0.037$, $\theta_2 = 0.114$, $\alpha = 0.018$, and $\beta = 0.016$ radian, $r = 2.32$ A, and $E(\text{total}) = 0.76$ kcal mole$^{-1}$.

The energy of the locked *gauche-n*-butane configuration may be calculated by setting $\theta_1 = \theta_2 = 0$. This leads to $\alpha = 0.029$ radian, $\beta = 0.027$ radian, $r = 2.20$ A, and $E(\text{total}) = 1.04$ kcal mole$^{-1}$.

The foregoing calculation may be refined somewhat

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by including bending strain due to deviations from their equilibrium values of the five other bond angles in each methyl and each methylene group, but the results are not much different. If $\gamma$ and $\delta$ are the deviations of the CCH and HCH angles, respectively, from their equilibrium values at the methylene carbon in *trans-n*-butane, then the total bending strain in each methylene group is $(k_\alpha\alpha^2 + 4k_\gamma\gamma^2 + k_\delta\delta^2)/2$. For small angles $\gamma = C\alpha$ and $\delta = D\alpha$, where $C = -k_\delta/(4k_\delta + k_\gamma)$ and $D = -k_\gamma/(4k_\delta + k_\gamma)$. Thus the bending strain is $k_\alpha'\alpha^2/2$, where $k_\alpha' = k_\alpha + 4k_\gamma C^2 + k_\delta D^2$. Taking $k_\gamma$ and $k_\delta$ as $6.84 \times 10^{-12}$ and $5.31 \times 10^{-12}$ erg radian$^{-2}$, respectively,[32] leads to $k_\alpha' = 12.13 \times 10^{-12}$ erg radian$^{-2}$. An analogous treatment of bending at a methyl carbon leads to an effective force constant $k_\beta'$ of $7.67 \times 10^{-12}$ erg radian$^{-2}$. With these higher effective bending force constants the results of energy minimization become $\theta_1 = 0.038$, $\theta_2 = 0.116$, $\alpha = 0.016$, and $\beta = 0.014$ radian, $r = 2.32$ A, and $E$(total) = 0.77 kcal mole$^{-1}$. For the locked configuration the results are $\alpha = 0.027$ radian, $\beta = 0.024$ radian, $r = 2.19$ A, and $E$(total) = 1.07 kcal mole$^{-1}$.

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# The Preparation and Properties of the Yellow Potassium Salt Containing Xenon in Oxidation States VI and VIII

**T. M. Spittler[1] and Bruno Jaselskis**

*Contribution from the Department of Chemistry, Loyola University, Chicago, Illinois.* *Received February 3, 1966*

**Abstract:** The yellow salt of the potassium-containing xenon in mixed oxidation states VI and VIII is prepared by mixing equal volumes of approximately 0.2 *M* xenon trioxide with 5.0 *M* potassium hydroxide and subjecting the solution to ozonolysis for 20 min. The resulting yellow salt corresponds to an apparent formula $K_4XeO_6 \cdot 2XeO_3$ (mol wt 742). This salt is explosive and very sensitive to a mechanical shock. However, it is thermally stable up to 201°. Above this temperature it is converted to a white anhydrous potassium perxenate salt.

Appelman and Malm[2a] have reported the formation of a yellow salt which they obtained by mixing concentrated potassium hydroxide with xenon trioxide. This salt has neither the properties of potassium perxenate nor the properties of alkali xenates as reported by Zalkin, *et al.*,[2b] and Spittler and Jaselskis,[3] respectively. Koch and Williamson[4] conclude from analysis of the potassium hydroxide–xenon trioxide system that the ratio of Xe(VI)/Xe(VIII) can vary between 4 and 0.1 when compared by algebraic difference to the total amount of xenon remaining in solution. However, we observe that the composition of the yellow salt is slightly affected by the precipitation conditions. A closer investigation of the yellow potassium salt has been undertaken and is reported in a later section.

## Experimental Section

**Chemicals and Apparatus.** Solutions of xenon trioxide were obtained from the Argonne National Laboratory. Approximately 0.25 *M* xenon trioxide solutions were employed for the preparation of potassium yellow salt. Reagent grade potassium hydroxide was used to prepare the 5.0 *M* hydroxide solution.

The infrared spectra were obtained of the yellow salt in a silver chloride pellet by the use of Perkin-Elmer 21, Perkin-Elmer 521, and KBr Infracord recording spectrophotometers. The X-ray powder diffraction patterns were obtained using a Norelco X-ray diffraction unit equipped with a 114-mm camera and Ni filter. The thermal stability was determined by use of differential thermal analysis apparatus. The collected gases, as a result of heating the yellow salt, were measured by the use of conventional vacuum-line techniques.

**Preparation of the Yellow Salt and Analysis.** In a typical preparation 1 ml. of 0.25 *M* xenon trioxide was mixed with 1 ml of 5.0 *M* potassium hydroxide. Ozone was bubbled through the solution for 20 min. The supernatant liquid was separated from the precipitate by decantation, and ozone again was bubbled through the solution until no further yellow precipitate resulted. The yellow salt was washed several times with water and dried gradually, bringing the temperature to 140°. The supernatant liquid was concentrated to about one-fourth of its original volume. On concentration a copious white potassium perxenate precipitate formed.

The yellow salt also can be prepared from ozone-free solutions by letting the solution stand for 12 to 24 hr. However, the oxygen-to-xenon ratio in the resulting salt is somewhat lower than in the ozonized product.

The ratio of oxygen to xenon as a result of heating the yellow potassium salt was obtained using the vacuum-line technique. A freshly precipitated sample of the yellow potassium salt was dried at 140° in all Pyrex system and pumped to $1 \times 10^{-3}$ mm. The sample chamber was slowly heated by means of a sand bath, and the pressure which remained between $10^{-5}$ and $10^{-4}$ mm up to 200° was monitored with a Miller gauge. At about 210° the pressure rose to 3 mm. The xenon gas was condensed and the oxygen transferred into a measuring volume by passage through a small U-tube trap held at nitrogen-slush temperature (−210°). After about 30 min of slow gas evolution and collection, the system pressure dropped to $1 \times 10^{-5}$ mm. The evolved oxygen was measured and discarded. The nitrogen-slush bath was removed from the trap and the evolved xenon was measured in the predetermined volume.

The amounts of xenon(VI) and xenon(VIII) in the yellow potassium salt were determined by the "hi-lo" titration as described by Appelman and Malm.[2a] Potassium was determined gravimetrically as potassium perchlorate after the decomposition of the yellow salt with aqueous methanol.

## Results

**Stability and Properties.** The yellow potassium salt once dried maintains constant weight and shows no tendency to absorb moisture, even at relatively high

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[1] On leave of absence from the Department of Chemistry, University of Detroit, Detroit, Mich.

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