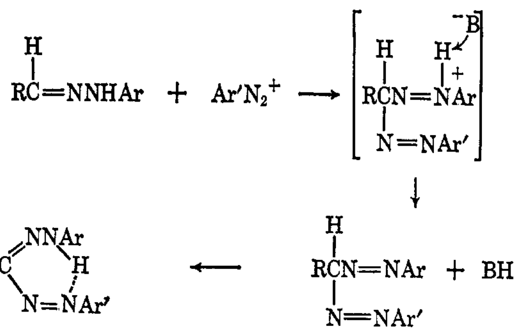
characteristic of the bis(arylazo)methane is observed.[4] Formation of the intermediate occurs most rapidly with the anion of the hydrazone, but the neutral molecule also has considerable reactivity. For this latter reaction the relative magnitudes of the ρ values obtained for substituent variation in the hydrazone and aldehyde rings compare with the reported[20] values for the bromination of hydrazones. Thus, even though the absolute magnitudes of the substituent responses, as measured by ρ values, are quite different for the two reactions, as expected since they involve different reagents and were measured under different solvent conditions, the ratio of the ρ values (3.4 for diazonium ion attack, 3.5 for bromination) obtained for both reactions are remarkably similar. This suggests a similar distribution of the available electronic charge along the hydrazone system in the transition states of both reactions.



Registry No.—$C_{13}H_{10}Cl_2N_2$, 6579-24-4; $C_{13}H_{11}BrN_2$, 10407-11-1; $C_{19}H_{16}N_2$, 1047-12-2.

Acknowledgment.—We are grateful to the Department of Education for financial support (State Maintenance grant to A. F. H.) and to Dr. Rubalcava, University College, Dublin, for the nmr spectra.

Substituent Electronegativity and the Thermodynamic Stabilities of Isomeric Substituted Propanes and Butenes

G. C. Robinson

Ethyl Corporation, Baton Rouge, Louisiana 70821

Received May 13, 1966

Literature data on equilibrium mixtures of isomeric substituted propanes and of isomeric substituted butenes have been summarized. The relative free energies derived from the propyl equilibria are to a first approximation linearly related to the Pauling electronegativity of the substituent atom bonded to the propyl system. A similar linear correlation is found for the butenyl system.

In organic reactions which may yield isomeric products, both kinetic and thermodynamic factors can influence product compositions. A knowledge of the relative free energies of the isomeric products fixes the equilibrium composition and is, therefore, of great value in planning synthetic procedures and in the analysis of kinetic data. In principle, relative free energies can be obtained from tabulated standard heats and entropies of formation of individual compounds from thermochemical measurements. In fact the precision demanded when thermochemical data are used for comparison of isomers often taxes, even now, the experimental techniques available. Much of the currently available data is too inaccurate for use in calculating relative free energies of isomeric substances.

A more direct, experimentally less demanding, procedure is to equilibrate the isomeric substances and to determine equilibrium composition as a function of temperature. Unfortunately, side reactions often frustrate attempts to reach equilibrium. In spite of the excellent early book of Parks and Huffman,[1] reports on such equilibria have been rare. In the past few years, however, useful equilibrium data have begun to appear in the literature, primarily on the propyl and butenyl systems. Examination of the available data has led us to propose a linear correlation between substituent electronegativity and relative free energies of isomers in these two systems which is useful for predicting equilibrium compositions.

In the isomeric monosubstituted propanes complete

$$CH_3CH_2CH_2X \rightleftarrows CH_2CHXCH_3$$

thermodynamic data from equilibrium measurements are available for chloro-[2] and bromopropanes.[3,4] Reliable thermochemical data are available for butane and isobutane[5] and an approximate equilibrium constant at one temperature is available for a di-*n*-propylboron substituent.[6] The data on the propyl alcohols are contradictory. A recent study of the heats of combustion of *n*-propyl and isopropyl alcohols[7] has given $\Delta H°$ (isomerization) as -2.98 ± 0.11 kcal/mole at 25° in the liquid phase, much less than the -5-kcal/mole value implied by direct measurements of the equilibrium between *n*-propyl and isopropyl alcohol[8,9] together with estimated entropies of isomerization.[10] The equilibrium measurements were in strongly acidic media and could be misleading. Pending experimental resolution of this conflict, preferably by vapor phase equilibrium measurements, no choice is made between the two results.

---

[1] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1932.

[2] G. Ya. Kabo and D. N. Andreevskii, *Neftekhimiya*, **5**, 132 (1965).

[3] A. M. Rozhnov and D. N. Andreevskii, *ibid.*, **4**, 111 (1964).

[4] H. S. A. Dowes and E. C. Kooyman, *Rec. Trav. Chim.*, **82**, 277 (1964).

[5] "Lange's Handbook of Chemistry," 8th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1952, p 1672.

[6] P. A. McCusker, F. M. Rossi, J. H. Bright, and G. F. Hennion, *J. Org. Chem.*, **28**, 2889 (1963).

[7] J. Chao and F. D. Rossini, *J. Chem. Eng. Data*, **10**, 374 (1965).

[8] S. Ehrenson, S. Seltzer, and R. Diffenbach, *J. Am. Chem. Soc.*, **87**, 563 (1965).

[9] V. Gold and R. S. Satchell, *J. Chem. Soc.*, 1938 (1963).

[10] J. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961).

TABLE I

THERMODYNAMIC DATA: n-PROPYL X → ISOPROPYL X AT 400°K

X	Registry no.	Electronegativity	σ(product)/ σ(reactant)	ΔH, cal/mole	ΔS, eu/mole	ΔG, cal/mole	ΔG_{chem}, cal/mole
Cl	540-54-5	3.0	3	−3200	−3.175	−1930	−2810
Br	106-94-5	2.8	3	−2900	−3.34	−1560	−2440
CH_3	106-97-8	2.5	4.5	−1640	−3.68	−160	−1360
H	74-98-6	2.1	1	0	0	0	0
OH	71-23-8	3.5	3	−2980 ± 110[a]	...	−3400 to −6000[b]	...
$(n\text{-Pr})_2B$	1116-61-6	2.0	1	...	...	+2430	+2430

[a] Reference 7. [b] References 8 and 9.

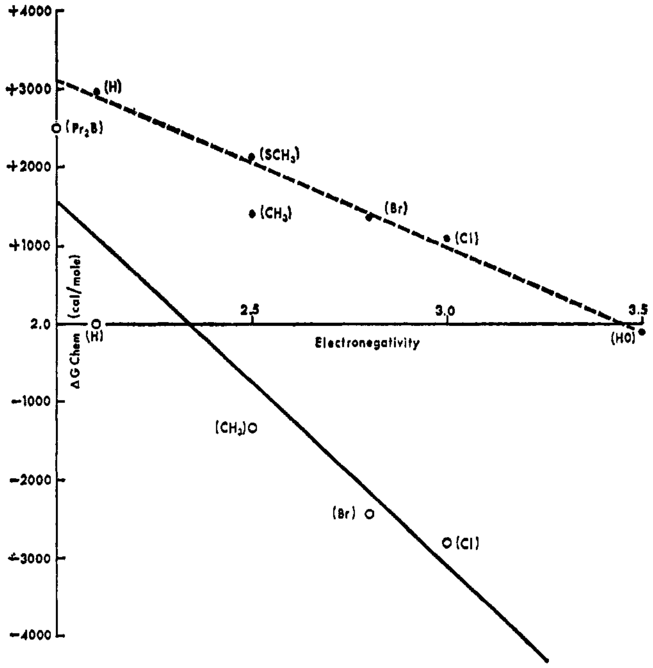


Figure 1.—Variation of free energies of isomerization with electronegativity for the rearrangements of n-propyl X to isopropyl X (400°K, open circles) and crotyl X to methylvinylcarbinyl X (353°K, solid circles).

The values of the various thermodynamic quantities for propyl equilibria are summarized in Table I along with the substituent electronegativities and the corrections[11] applied to the free-energy values to remove incidental symmetry and entropy of mixing effects. The free energies are calculated at 400°K where the equilibrium constant for the di-n-propylboron substituent is known. The propane-to-propane identity is included in this table.

Equilibria are more readily established in the crotyl-methylvinylcarbinyl systems, so results are available

$$CH_3CH{=}CHCH_2X \rightleftarrows CH_3CHXCH{=}CH_2$$

for more substituents. Unfortunately these data are largely in the liquid phase and at a single temperature. In Table II the usable literature data are collected along with the substituent electronegativities and the appropriate symmetry corrections. Extrapolation of ΔG (isomerization) values to a common temperature (353°K) without entropy data was necessary in compiling this table. Since the extrapolations were short no correction was made to the primary data.

TABLE II

THERMODYNAMIC DATA:
CROTYL X → METHYLVINYLCARBINYL X AT 353°K

X	Electronegativity	σ(product)/ σ(reactant)[a]	ΔH, cal/mole	ΔS, eu/mole	ΔG, cal/mole	ΔG_{chem}, cal/mole
CH_3[b]	2.5	1	+670	−2.11	+1410	+1410
SCH_3[c]	2.5	0.50	...	...	+1635	+2120
H[d]	2.1	0.17	+3100	+3.6	+1680	+2940
Cl[e]	3.0	0.50	...	...	+600	+1090
Br[f]	2.8	0.50	...	...	+870	+1360
OH[g]	3.5	0.50	...	...	−620	−130

[a] Reference 11. [b] Reference 4, p 1684. [c] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 2867 (1965). Measured at 308°K. [d] S. W. Benson and A. K. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963). [e] D. C. Dittmer and A. F. Marcantonio, *J. Org. Chem.*, **29**, 3473 (1964). [f] W. G. Young, *et al.*, *J. Am. Chem. Soc.*, **61**, 3070 (1939). Measured at 373°K. [g] G. W. Hearne and D. S. LaFrance, U. S. Patent 2,373,956 (April 17, 1945); W. G. Young and J. S. Franklin, *J. Am. Chem. Soc.*, **88**, 785 (1966). Measured at 368°K.

Inspection of Tables I and II suggests a correlation between substituent electronegativity and free energies of isomerization. In Figure 1 the ΔG_{chem} values are plotted against Pauling electronegativities. Both sets of data show a linear trend toward increasing stability of the secondary isomer with increasing substituent electronegativity.

The fit of the data to a linear relationship is fair for the propyl systems. Since the free-energy values plotted, except for a hydrogen substituent, are affected by a roughly constant entropy term, a better test of the linearity hypothesis using the propane-to-propane identity isomerization as an absolute point requires plotting ΔG_{chem} at 0°K, *i.e.*, ΔH(isomerization) *vs.* Pauling electronegativity. This was done in Figure 2 using the limited available data. It is evident that a good linear relationship is obtained except for the hydroxy substituent. In view of the previously discussed uncertainty about this ΔH(isomerization) and the marked departure from the trend of the other data, we have ignored the hydroxy point in drawing the line. The predicted value of ΔH(isomerization) for a hydroxy substituent using the line is −5300 cal/mole, about 2000 cal/mole more negative than the results of Chao and Rossini would suggest. Equilibrium data on the propyl fluorides[12] would be very helpful in testing the linearity hypothesis.

Referring again to Figure 1, one notes that the butenyl systems fit a linear correlation quite well. In this case the hydroxy substituent gives no problem, it falls on the correlation line. The butenyl correlation line lies well (2–3 kcal/mole) above the propyl correlation in part because the interior double bond in the crotyl isomer is stabilized relative to the terminal double bond of the methylvinylcarbinyl isomer.

[11] We are grateful to a referee for pointing out the necessity for these corrections; *cf.* S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

[12] The literature value of ΔH isomerization for the fluorides is −1.77 kcal/mole but may be in substantial error: J. R. Lacher, A. Kianpour, and J. D. Park, *J. Phys. Chem.*, **60**, 1454 (1956).

The equation of the line in Figure 1 for the propyl system at 400°K is

$$\Delta G_{\text{chem}} = -4660E + 10{,}850$$

where E is the Pauling electronegativity. Similarly, the equation of the line for the butenyl system at 353°K is

$$\Delta G_{\text{chem}} = -2130E + 7380$$

Using these equations one would predict for an aluminum propyl system ($E = 1.5$) a ΔG_{chem} of +3850 cal/mole; *i.e.*, *n*-propylaluminum should be substantially more stable than isopropylaluminum. For magnesium ($E = 1.2$) ΔG_{chem} would be +4260 cal/mole. Although no quantitative data are available on these systems, qualitatively it is known that both aluminum[13,14] and magnesium[15] are most stable at a primary site. For a butenylmagnesium system, ΔG_{chem} is predicted to be +4820 cal/mole. Whitesides, Nordlander, and Roberts[16] have deduced from nmr data that butenylmagnesium bromide is predominantly the crotyl isomer as predicted.

Of particular interest is the isomerization free energy for *n*-propyllithium to isopropyllithium. Using an average entropy of isomerization of −3.3 eu and adding the symmetry correction to ΔG_{chem}, one calculates a directly observable isomerization free energy of +5000 cal/mole corresponding to log $K_{\text{eq}} = -3.64$. This value can be compared with the McEwen–Streitwieser–Applequist–Dessy (MSAD) pK_{a} scale of Cram.[17] If one assumes that pK_{a} for a primary propyl hydrogen is the same as for ethane, the log E_{eq} predicted by Cram is −2 while the present correlation gives −3.64 as cited above. This result suggests that the upper end of the MSAD scale may be slightly compressed.

A diverse family of correlations similar to the two presented in this paper can be expected. In purely aliphatic systems a primary–tertiary and a secondary–tertiary correlation should exist. Functional groups of all types will require their own correlations for substituents at adjacent positions. However, given the knowledge that a correlation probably exists, determination of a few equilibrium constants will permit a rational extrapolation to a variety of substituents.

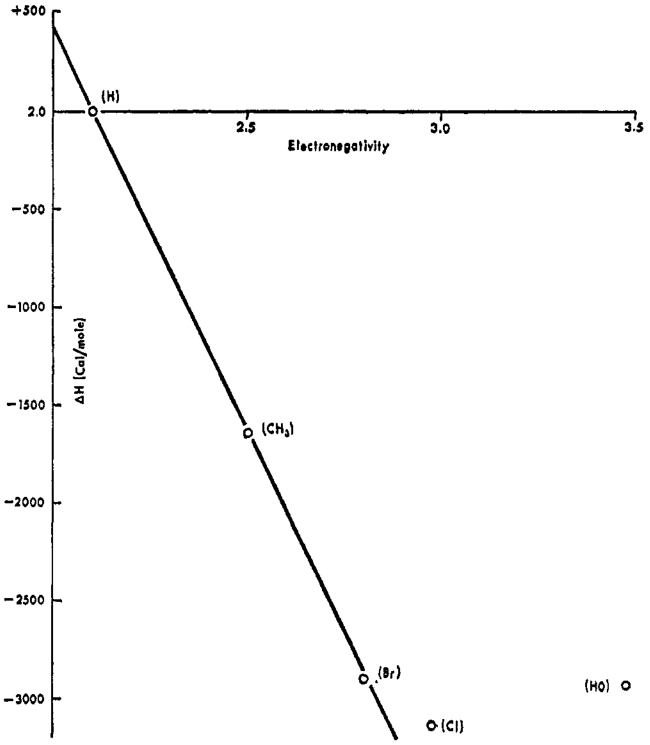


Figure 2.—Variation in enthalpy of isomerization with substituent electronegativity for *n*-propyl X to isopropyl X.

When using these linear relationships between free energies and electronegativity, their limitations should be remembered. They are empirical,[18] and extrapolation to extremes of electronegativity is uncertain. Formation of dimers, trimers, etc. may substantially complicate the equilibria for metal alkyls in the condensed state.[19] Changes in bond strength as well as electronegativity may affect the equilibria. Also electronegativity is a function of the state of bonding of an atom as well as of the atom. One would not, for example, expect exactly the same equilibrium constant for butane–isobutane as for *n*-propylbenzene–cumene. In fact the differences observed in such closely related equilibria may generate a more detailed electronegativity scale than is currently available. Comparison of such scales with calculated orbital electronegativities would be of theoretical interest.[20]

It is hoped that this paper will stimulate the systematic collection of equilibrium data on simple isomeric systems. Such data are extremely useful.

---

(13) F. Asinger, B. Fell, and R. Jansen, *Ber.*, **97**, 2515 (1964).

(14) G. Bruno, Abstracts of Papers, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 19–24, 1964, p 24C.

(15) G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, **27**, 1497, 3395 (1962).

(16) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2010 (1962).

(17) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 19.

(18) A referee has pointed out that assuming different electronegativities for *n*-propyl and for isopropyl (or crotyl and methylvinylcarbinyl) would, together with the Pauling bond energy equation, predict a linear relation between substituent electronegativity and ΔH (isomerization); *cf.* W. F. Sager and C. D. Ritchie, *J. Am. Chem. Soc.*, **83**, 3498 (1961).

(19) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

(20) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, **85**, 148 (1963).