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The Anomalous Strength of *n*-Butyric Acid

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Thermodynamic dissociation constants[1] are now available for the saturated aliphatic *n*-acids extending from formic to nonoic acid and the following features have become apparent. In the first place there is a very pronounced fall in dissociation constant in going from formic to acetic acid. Second, although the general trend is for the acid strength to diminish as the alkyl chain lengthens and to approach a limiting value in the higher members of the series, there is a distinct increase in K in proceeding from propionic to *n*-butyric acid, and it has been suggested[1a] that this enhancing influence still persists in the succeeding *n*-acids (elevation of the dissociation constant being attributed to some interaction between the hydrogens of the γ-carbon and the carboxyl group). Further consideration is now given to this anomaly.

Undoubtedly some correlation exists between the length of the alkyl chain and the corresponding acid strength. For a working hypothesis we shall be concerned with the distance separating the carbon of the carboxyl group and the terminal carbon atom, or the terminal hydrogen in the case of formic acid. Table I gives these distances r (the carbon–carbon valency angle being taken as 109° in propionic acid) and the dissociation constants for the first three members of the series.

TABLE I

Acid	r (A)	$1/r^6$	$10^5\ K$	$5 + \log K$
Formic	1.06	0.705	17.72	1.248
Acetic	1.54	0.075	1.75_5	0.244
Propionic	2.54	.004	1.33_5	.125

The distances are unambiguous, that is, they are not affected by the presence or absence of free rotation, and a plot of log K against $1/r^6$ reveals linearity (see Fig. 1). Moreover, a relation of this type predicts a limiting value for the dissociation constant of a *n*-aliphatic acid as the alkyl chain lengthens. The equation to the line using Napierian logarithms is $\ln K = a + b/r^6$ where b has the value 3.7×10^{-48} in absolute units; this approximates to $N\alpha_0\mu^2/RT = 10^{-46}$ where N is the Avogadro number, R the gas constant, T the absolute temperature if α_0, the polarizability of the carbon–carbon bond, is taken as 0.5×10^{-24} and μ, the inducing dipole, as $2D$.

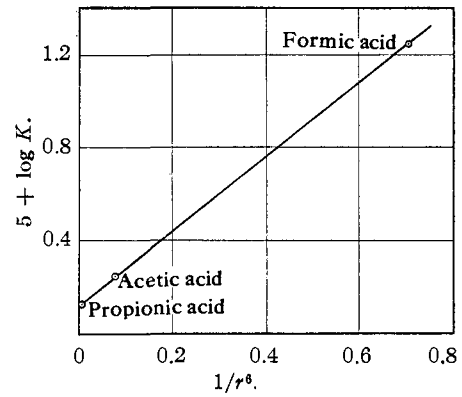

Fig. 1.

Now proceeding to *n*-butyric acid and higher members of the series, we are confronted with the possibility that free rotation moves the γ-carbon atom from one extreme of a *cis* position, where it is in close proximity to carboxyl, to the other extreme of a *trans* position. An average distance is evidently needed and we shall use $(\bar{r}^2)^{1/2}$ the root mean square distance between the ends of the structure; this has been calculated for *n*-butyric acid to be 3.36 Å. by the method of Eyring,[2] assuming complete free rotation about the valence bonds and no distortion of valency angles. The formula is

$$\bar{r}^2 = c_1^2\{n + 2(n - 1)\cos\theta + 2(n - 2)\cos^2\theta \ldots + 2\cos^{n-1}\theta\}$$

where c_1 is the distance between consecutive carbon atoms and is the supplement of the carbon–carbon valency angle, taken as 109°. However, since this distance in the *n*-butyric acid molecule is larger than the corresponding distance in the propionic acid molecule, while K for butyric acid (1.50×10^{-5}) is also larger than that for propionic acid ($1.33_5 \times 10^{-5}$), clearly *n*-butyric acid is anomalous, using the linear relation as criterion. To bring butyric acid into conformity with the linear relationship, the distance r (as determined by graphical interpolation) should be 1.8 Å. and not 3.36 Å. as calculated from Eyring's formula. Two suggestions can be made as

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[1] (a) Dippy, *J. Chem. Soc.*, 1222 (1938); (b) Harned, *et'al.*, THIS JOURNAL, **55**, 652, 2379 (1933); (c) **56**, 1042, 2039 (1934).

[2] Eyring, *Phys. Rev.*, (2) **39**, 746 (1932).

to how the effective distance is decreased. First, the hypothesis of completely unhindered rotation in the *n*-butyric acid molecule may be abandoned. A consideration of the geometry of the system reveals that the minimum distance of approach of the terminal carbon atom to the carbon atom of the carboxyl group is considerably less than the root mean square value and equal to 2.5 Å.; thus it seems very likely that the rotation is practically frozen in the *n*-butyric acid molecule which thus exists in a "*cis*" configuration. In this connection it should be noted that the strengths of simple monobasic olefinic acids of the *cis* configuration are always greater than their *trans* isomers; this is well illustrated by the crotonic acids (10^5 *K; trans* 2.03, *cis* 3.6) which have a carbon system comparable to *n*-butyric acid. Furthermore, there is now considerable evidence of restricted rotation about a single bond, derived from dipole moment, infrared absorption spectra, Raman spectra and heat capacity studies; for instance, in the case of formic acid Bauer and Badger[3] have reason to believe that the hydroxyl group is firmly established in the *cis* position. A *cis* configuration for butyric acid is favored by the facts that the C–CH_3 and C–O dipoles are of opposite sign and that their mutual potential energy is greater than kT, the energy of thermal agitation. It is likely nevertheless that in order to account adequately for the complete restriction of rotation, other influences beside dipole attraction will have to be taken into consideration, such as the London attraction which has been used by Weissberger to explain the dipole moments of disubstituted diphenyl derivatives, and the fact that *cis*-dichlorethylene is the more stable[4] of the two isomerides at 300°. The dipole attraction, however, must play a part, and be less potent the higher the temperature. As the temperature is raised, therefore, we would expect the dissociation constant of butyric acid to fall; Harned and Sutherland[5] record the temperature of maximum K for butyric acid as 8°, whereas for acetic, propionic, and other acids[6] differing in strength by more than an order of 10, the corresponding values lie between 20 and 25°. Thus we have in *n*-butyric acid some factor entering which influences the "normal" temperature change of K exemplified by acetic acid and propionic acid, and at the same time the butyric system is the first in the homologous series in which the extent of freedom of rotation determines the effective distance r. Since this complicating factor of the existence of a restricting potential must occur in all the higher fatty acids extending from *n*-butyric acid, their strengths must be abnormally high. As a further consequence of this valeric and isovaleric acids should show a temperature dependence of K similar to that of *n*-butyric acid and not to propionic acid. Work on this problem is now proceeding.

Again, another factor which helps to reduce the effective distance in the *n*-butyric molecule is the extreme flexibility of the four carbon system compared with that obtaining in the three carbon system of propionic acid. An electron diffraction investigation of the valency angles in the *n*-butyric molecule would contribute materially to the solution of the anomaly of this acid.

Summary

A linear relationship has been discovered between the logarithms of the dissociation constants of formic, acetic and propionic acids, and the inverse of the sixth power of r, the distance separating the carbon of the carboxyl and the terminal group of the acid. This relationship predicts a limiting value for the higher acids. The slope of the line shows good agreement with a theoretical expression. As a deduction from this relationship the abnormality already recognized to exist in *n*-butyric acid has been interpreted in terms of the existence of a restricting potential in the molecule; this is in harmony with conclusions reached in infrared absorption, Raman spectra, heat capacity, and dipole moment studies.

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[3] Bauer and Badger, *J. Chem. Phys.*, **5**, 852 (1937).

[4] Ebert and Bull, *Z. physik. Chem.*, **152A**, 451 (1931); Stuart, *Physik. Z.*, **32**, 793 (1931).

[5] Harned and Sutherland, THIS JOURNAL, **56**, 2039 (1934).

[6] Nims, *ibid.*, **58**, 987 (1936); Martin and Tartar, *ibid.*, **59**, 2672 (1937).