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W. BENCZE und H. SCHMID

Chemisches Institut der Universität Zürich, den 12. August 1953.

Summary

The structure of Visamminol (I), a compound isolated from *Ammi visnaga* by SMITH, PUCCI, and BYWATER, has been elucidated by degradation and by a comparison of the UV.-spectra of I and its derivatives with those of other chromones.

The Effect of Hyperconjugation upon the Boiling Points of Alkenes

The boiling point is conceived as the perceptible manifestation of the underlying physical phenomenon of inter-molecular attraction, called cohesion (Kohäsion) by HÜCKEL[1]. As such it is a function of the degree of electrical asymmetry of the molecule. This asymmetry of charge distribution is known to be the sum of two effects: the permanent or orientation polarization ($P\mu$), and the induced polarization (P_D) or "polarizability".

By applying these principles, HÜCKEL has been successful in formulating qualitative correlations between the structures and boiling points of organic compounds, now well-known as "HÜCKEL's boiling-point rules". There remain, however, some cases in which these rules, in their present form, fail to rationalize the factual evidence. Thus HÜCKEL recognized an increase in boiling point with increasing proximity of an alkyl group to a carbon-carbon double bond. Generally, the boiling point *decreases* with increasing proximity of an alkyl group to a polar (e.g. carbonyl) function, and this so-called "shielding effect" is explained by steric inhibition of polarizability by the bulky and only weakly polar alkyl radical. HÜCKEL was unable to explain why this principle seemed to fail in the case where the polar group is a point of carbon-carbon unsaturation. Similarly, irregularities have been noted[2] in that the normal 1-olefins which would be expected to be the highest boiling by virtue of their extreme asymmetry (maximum $P\mu$), actually have lower boiling points than any of their C=C position isomers. There is no rational interpretation of this behavior at the present time.

Now it is clear that the structures of two or more aliphatic or alicyclic mono-olefins differing structurally only in the position of the carbon-carbon double bond (but not in their carbon skeleton) can differ only in their electron distribution, and that the latter must manifest itself in one of the following ways:

(1) in the permanent polarization, $P\mu$

(2) in the induced polarization, P_D, by means of either

(I) shielding effects of bulky groups preventing small inter-molecular distances and thus decreasing the effective polarizability, or

(II) intrinsic differences in the degree of electron delocalization which could, depending on their nature, decrease or increase effective polarizability.

As (1) and (I) do not account for the observed facts but are actually in contradiction to them, only (II) can provide a clue. Reflection will show that there must indeed be a difference in electron delocalization of C=C isomeric olefins inasmuch as they differ in the amount of hyperconjugation possible in the respective structures.

To test the resulting hypothesis, namely that hyperconjugation will have a measurable effect upon the boiling point of unsaturated hydrocarbons, a statistical analysis of some hundred compounds was undertaken. The compounds chosen comprise all the aliphatic mono-olefins from C_4 to C_7, inclusive, which are capable of C=C position isomerism; the n-octenes and methyl-heptenes; and the normal alkynes from C_4 to C_6, inclusive. The only principle governing this selection was easy accessibility of boiling point data, which were obtained from the best current sources[1]. The number of hydrogen atoms in α-position with respect to the double bond served as a convenient quantitative means of expressing the "amount" of hyperconjugation. A representative sample will illustrate the methods used (Table).

[1] W. HÜCKEL, *Theoretische Grundlagen der Organischen Chemie* (Akademische Verlags-GmbH., Leipzig, 1935), 2nd ed., 2nd vol., p. 122.

[2] J. A. LEERMAKERS and A. WEISSBERGER in H. GILMAN, *Organic Chemistry* (Wiley, New York, N.Y., 1943), p. 1723.

[1] F. D. ROSSINI *et al.*, *Selected Values of Properties of Hydrocarbons* (National Bureau of Standards, Circular C 461, U. S. Government Printing Office, Washington, D.C., 1947). – G. EGLOFF, *Physical Constants of Hydrocarbons* (Reinhold Publishing Corp., New York, N. Y., 1953, Volume V).

Compound	Structure	Hyperconjugation	Boiling Point at 760 mm
5-Methyl-1-hexene	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH=CH_2$	2	85·650
2-Methyl-3-hexene	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH-CH_2-CH_3$	3	86°
5-Methyl-2-hexene	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH=CH-CH_3$	5	*cis:* 91° *trans:* 86°
2-Methyl-1-hexene	$CH_2=\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CH_2-CH_2-CH_2-CH_3$	5	91·3°
2-Methyl-2-hexene	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH-CH_2-CH_2-CH_3$	8	95·41°

The coefficient of rank correlation was computed for each group of isomers, using SPEARMAN's formula:

$$r = 1 - \frac{6\,\Sigma\,(x-y)^2}{n^3-n}$$

where r is the coefficient of rank correlation, x and y are the rank positions of the two variables, and n is the number of members in each series. For the sample given, $r = 0{\cdot}975$. The sample illustrates various causes of imperfect correlation which are inherent in the nature of the data:

Several structures may have the same amount of hyperconjugation and still differ in their boiling points due to determining factors not considered in the present analysis; and boiling points of structures which give rise to *cis-trans* isomerism are difficult to arrange in order of rank. Occasionally, only the boiling point of steric mixtures is recorded; where boiling points of sterically pure isomers are available, it is impossible to choose either one in fairness as the difference between them is unrelated to hyperconjugation and probably due to a change in $P\mu$.

Nevertheless, the correlations calculated as shown are equal to one in most, and higher than 0·8 in all series studied. The deviations which do exist can invariably be traced to difficulties such as those mentioned above. More important, in spite of these difficulties, the probability of the null hypothesis (i.e. the hypothesis that there is no dependency between hyperconjugation and boiling point in the compounds concerned) can be calculated by standard statistical methods to be in the order of 10^{-25}, or definitely negligible.

Concluding, a positive effect of hyperconjugation upon the boiling points of aliphatic mono-olefins may be considered established. The magnitude of this effect is such that it completely supersedes that of symmetry of charge distribution in these weakly polar (i.e. essentially quadrupolar) molecules. It is to be expected that analogous relationships can be found in other classes of organic compounds.

C. W. BECK

Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A., August 23, 1953.

Zusammenfassung

Es wird gezeigt, dass die Hyperkonjugation einen entscheidenden Einfluss auf den Siedepunkt der einfach ungesättigten aliphatischen Kohlenwasserstoffe hat. Dieser Zusammenhang wird durch vergrösserte Elektronendelokalisierung in Molekülen, die Hyperkonjugation aufweisen, theoretisch verständlich. Ein grösseres Ausmass der Elektronendelokalisierung führt zu stärkerer Kohäsion und dadurch zu erhöhten Siedepunkten. Die neue Gesetzmässigkeit ergänzt ohne Widerspruch die bekannten Hückelschen Siedepunktsregeln und erklärt Beobachtungen, die aus keiner der bisher aufgestellten Regeln ableitbar waren. Es ist zu erwarten, dass analoge Zusammenhänge in anderen Gruppen von organischen Verbindungen aufgewiesen werden können.

Zur bakteriziden Wirkung von komprimiertem Sauerstoff

Es ist bekannt, dass Sauerstoff unter Druck das Wachstum aller Mikroorganismen hemmt[1]. Dieser bakteriostatische Effekt wird bei längerer Einwirkungszeit und mit steigender Temperatur bakterizid[2]. Worauf diese keimabtötende Wirkung beruht, ist bisher ungeklärt. Toxische Stoffwechselprodukte können, wenn sie überhaupt auftreten, das Phänomen nicht erklären, da nach Beseitigung des Druckes das Wachstum sofort wieder einsetzt. Es ist weiter bekannt, dass komprimierter Sauerstoff die Atmung und den Stoffwechsel von Mikroorganismen in starkem Masse beeinträchtigt[3]. Daher liegt die Vermutung nahe, dass die Bakterien in ihrer Nährlösung verhungern, weil sie nicht in der Lage sind, die gebotenen Nährstoffe zu verwerten. Um diese Frage zu klären, wird *Escherichia coli* in flüssigem Nährsubstrat gezüchtet, abzentrifugiert, gewaschen und 24 h in physiologischer Kochsalzlösung bebrütet, um vorhandene Reservestoffe zu verbrauchen. Anschliessend setzt man die eine Hälfte der Bakterienaufschwemmung in «Standard-Merck-I-Bouillon» unter 8 atü O_2 und belässt den Rest unter gewöhnlichen Bedingungen in der physiologischen NaCl-Lösung. Die Bakterien sterben unter komprimiertem Sauerstoff schneller ab als in der Kochsalzlösung (siehe Abb.). Erhitzt man Coli-Bakterien kurzfristig auf höhere Temperatur, so ist die Absterberate unter 8 atü O_2 stets grösser als unter gewöhnlichem Luftdruck (Tab.). Aus diesen Gründen scheint ein Verhungern nicht die Ursache der bakteriziden Wirkung zu sein.

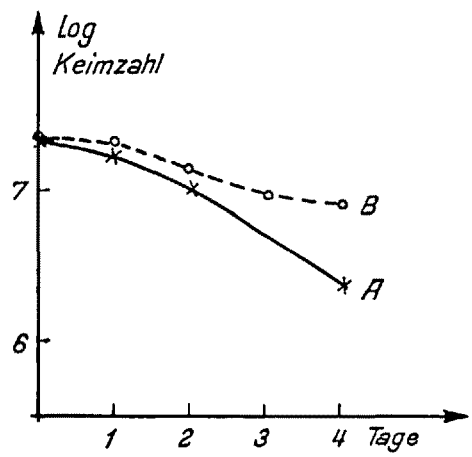

Abb. 1. Abnahme der Keimzahlen von *Escherichia coli* bei 26°C. *A* unter 8 atü O_2 in «Merck-I-Bouillon»; *B* unter gewöhnlichem Luftdruck in physiologischer Kochsalzlösung.

Es erhebt sich weiter die Frage, ob irreversible Fermentschädigungen für den bakteriziden Effekt verantwortlich sind. Wenn diese Möglichkeit auch nicht ganz auszuschliessen ist, so ist sie als alleinige Erklärung unzureichend. Hydrolytisch wirkende Fermente werden nicht so stark gehemmt wie dehydrierende Enzyme. Die

[1] N. CHUDIAKOW, Zbl. Bact., 2. Abtlg. *4*, 391 (1898). – C. FOA, Atti R. Acad. Lincei *15*, 185 (1906); Zbl. Bact. 1. Abtlg. Ref. *40*, 185 (1907). – BERGHAUS, Arch. Hygiene *62*, 172 (1907). – H. LÜCK, Schweiz. Z. Path. allg. Bakt. *16*, 728 (1953).

[2] H. LÜCK, Schweiz. Z. Path. allg. Bakt. *16*, 728 (1953).

[3] L. MASSART, Arch. int. Pharmacodyn. Thérap. *60*, 48, 56 (1938). – PH. J. LUTERAN, M. LANGERON und J. MERY, C. r. Acad. Sci. *228*, 338 (1949). – H. LÜCK, Schweiz. Z. Path. allg. Bakt. (im Druck).