are luminous even when travelling through a very high vacuum such as it exists in interplanetary space[1].

F. ZWICKY

California Institute of Technology, Pasadena, California, February 22, 1954.

Zusammenfassung

Gewöhnliche Explosivmittel und Raketentriebstoffe entwickeln nach Zündung Reaktionswärmen, welche den Wert $q_v = 3$ kcal je cm^3 nicht überschreiten. Dies gilt besonders für Kombinationen, die nur Kohlenstoff, Wasserstoff, Stickstoff und Sauerstoff enthalten. Da die Reaktionsprodukte solcher Triebstoffe alle gasförmig sind, geht im wesentlichen die Sublimationswärme der ursprünglich festen Stoffe verloren, und die Werte von q_v erscheinen entsprechend niedriger. Im gleichen Sinne wirkt die relativ leichte Dissozierbarkeit von CO, CO$_2$ und H$_2$O bei den resultierenden Explosionstemperaturen. Um grössere Werte von q_v zu erzielen, müssen deshalb Elemente, wie Lithium, Bor, Magnesium, Aluminium und Silizium, in die Explosivstoffe eingebaut werden, die nach Detonation feste und flüssige Oxyde und Verbindungen liefern. Es wird an Hand einiger Beispiele gezeigt, dass auf diese Weise Energiemengen verfügbar werden, die im Bereich von 4 bis 7 kcal je cm^3 liegen. Zur praktischen Ausführung können die genannten Leichtelemente entweder physikalisch einem gewöhnlichen Explosivstoff beigemischt werden, oder es können diese Elemente mit Wasserstoff, Stickstoff und eventuell Sauerstoff, Fluor usw. zur Verbindung gebracht und mit einem zusätzlichen Oxydationsmittel reagiert werden. Falls man in explosiven Hohlladungen potentiell selbstreagierende Einlagen aus komprimiertem Thermit oder ähnlichen Kompositionen benutzt, werden nach Detonation glühende Teilchen grosser Geschwindigkeit und grosser Durchdringungsfähigkeit ausgeschleudert. Diese Teilchen können auch als in einem Vakuum wie dem interplanetarischen Raum selbstleuchtende künstliche Meteore zu Experimenten verschiedener Art benutzt werden[2].

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[1] F. ZWICKY, Engineering and Science Monthly, Calif. Inst. of Technology, Pasadena, January 1953.

[2] G. BIRKHOFF, D. M. MACDOUGALL, E. M. PUGH and G. TAYLOR, J. Appl. Phys. *19*, 563 (1948).

The Relative Stabilities of *Cis* and *Trans* Isomers

The original rule for determining from physical properties which isomer in a cyclic system was *cis* and which was *trans* was proposed by VON AUWERS[1]. Unfortunately, this rule was found not to hold true in several cases and much confusion has been caused thereby. Most of these cases in which the rule of VON AUWERS fails to predict the isomers correctly show a consistency, a consideration of which has prompted a restatement of the original rule. With respect to *cis* and *trans* isomers in cyclic systems, *that isomer which has the highest boiling point, highest index of refraction and highest density is the isomer which possesses the least stable configuration.* It is apparent that the structures predicted by this rule will differ from those predicted by VON AUWERS rule only when the *trans* isomer is less stable than the *cis*.

The rule stated above is substantiated by an amount of experimental evidence which is too large to be discussed here except for certain cases of particular importance. It need only be said that of the hydrocarbons listed in various compilations[1], no exception to the rule was found[2]. Compounds containing functional groups were not exhaustively considered, but out of some dozen cases examined the predictions of the rule were confirmed with only one questionable case[3].

Three critical cases may be specifically mentioned. *cis*-1, 3-Dimethylcyclohexane is known[4] to be more stable than the *trans* isomer, and it was also recently shown that the same is true of the 1, 3-dimethylcyclopentanes[5]. A somewhat different type of system, [0, 3, 3]-bicyclooctane, also has a more stable *cis* isomer in contrast with the homologous hydrindanes[6] and decalins. In each of these cases the correct structures are predicted by the rule stated.

Although there is little evidence available[1] to support the contention, it is reasonable to suppose that the rule will apply to more highly subsituted systems and likewise to small- and large-ring compounds, and will thus be of practical value since the relative stabilities of the compounds can be determined in most cases by conformational analysis[7].

The existence of the rule stated above can be rationalized by qualitative theoretical considerations. An ideal case is a pair of simple *cis* and *trans* isomers of a cyclic saturated hydrocarbon. In such a case the forces acting in and between the molecules are quite similar and the differences in the physical properties of the compounds are due to a minimum number of differences in the forces acting. In this case it is evident that the isomer which has the greatest density and the greatest index of refraction has these properties as a result of its smaller molecular volume. It is equally true, if less obvious, that the smaller molecular volume leads to the higher boiling point[8] since the smaller molecular volume increases the magnitude of the dispersion forces which in turn leads to an increased heat of vaporization. The smaller molecular volume also requires the crowding together of the atoms within the molecule and, because of the internal repulsive forces encountered, a lower stability results. The rule stated is evidently a direct result of these effects and it may thus be determined what kinds of circumstances are required to cause the rule to fail.

An olefinic double bond may be considered in a formal sense as a two-membered ring and as such should also fit the rule. Consequently, the properties of some dozens of mono-olefinic hydrocarbons were considered[9] and, although in many cases the data are of insufficient accuracy to be definitive, no clear cut contradictions were found. Of particular interest are the isomers of

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[1] K. VON AUWERS, Ann. Chem. *420*, 84 (1920).

[1] G. EGLOFF, *Physical Constants of Hydrocarbons* (Reinhold, New York, N.Y. – J. S. FARADAY, *Encyclopedia of Hydrocarbon Compounds* (Chemindex, Manchester, 1945–52). – A. P. I. Tables, National Bureau of Standards.

[2] Account must be taken of the fact that some of the compounds listed as *cis* in the tables have since been shown to be *trans* and vice versa.

[3] A. SKITA and R. RÖSSLER, Ber. dtsch. chem. Ges. *72*, 265 (1939).

[4] C. W. BECKETT, K. S. PITZER, and R. SPITZER, J. Amer. Chem. Soc. *69*, 2488 (1947).

[5] S. F. BIRCH and R. A. DEAN, J. Chem. Soc. *1953*, 2477.

[6] W. HÜCKEL, Ann. Chem. *533*, 1 (1937).

[7] D. H. R. BARTON, J. Chem. Soc. *1953*, 1027.

[8] T. W. RICHARDS, Trans. Faraday Soc. *24*, 111 (1928).

[9] G. EGLOFF, *Physical Constants of Hydrocarbons* (Reinhold, New York, N.Y. – J. S. FARADAY, *Encyclopedia of Hydrocarbon Compounds* (Chemindex, Manchester, 1945–52). – A. P. I. Tables, National Bureau of Standards.

cyclooctene[1], cyclononene[2], and cyclodecene[3]. From the published physical constants the rule predicts that with the eight-membered ring the *cis* isomer would be the more stable, while the reverse would be true in the ten-membered ring and the isomers in the nine-membered ring would have nearly equal stabilities. The same orders of stability were found by chemical methods.

It is to be noted, however, that applications of the rule to olefins can be made with certainty only with mono-olefinic hydrocarbons. The reason for this limitation is that a double bond possesses electronic properties not shared by the other ring compounds and, in the presence of certain functional groups, interactions can occur which will overshadow the differences in the dispersion forces. As an example, 2-alkenoic acids are, as a class, known to be exactly reversed from the hydrocarbons with respect to the properties previously mentioned.

N. L. ALLINGER

Department of Chemistry, University of California, Los Angeles 24, California, February 26, 1954.

Zusammenfassung

Eine Neufassung der von-Auwerschen Regel ist vorgeschlagen worden. Die neue Regel ist auf *cis-* und *trans-*Isomeren gewöhnlicher zyklischer Systeme sowie auch auf mehrfach substituierte zyklische Verbindungen, polyzyklische Verbindungen und Olefine anwendbar. Das Bestehen einer solchen Regel ist begründet, und ihre Begrenzungen und praktischen Auswertungen sind unter Betracht gezogen worden.

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[1] K. ZIEGLER and H. WILMS, Ann. chem. *567*, 1 (1950).

[2] A. T. BLOMQUIST, L. H. LIU, and J. C. BOHRER, J. Amer. Chem. Soc. *74*, 3643 (1952).

[3] A. T. BLOMQUIST, R. E. BURGE, Jr., and A. C. SUCSY, J. Amer. Chem. Soc. *74*, 3636 (1952).

On the Chemical Nature of Acerin and the Virucidal and Antiviral Effects of Some Vegetable Tannins[1]

In a search for virucidal and antiviral substances in nature, one of us (G.F.) in 1952[2] found that water extracts of several plants exerted a definite virucidal effect, the main experiments being performed with a bacterial virus and its host cell, *Escherichia coli* XP. Out of 300 different plant species investigated, the majority yielded no activity, whereas fairly active extracts were obtained from some of them.

In his next communication, FISCHER[3] reported on the virucidal and antiviral effect of maple fruit preparations. 25 g of maple fruits gave 1 g of a substance, which in a dilution of 1:64 destroyed the bacterial virus in 5 min. The substance was given the name *acerin.*

Acerin also destroyed vaccinia virus in 5 min; its effect on the Staphylococcus Twort virus was much less pronounced.

After further purification (FISCHER[1]) whereby 100 g of maple fruits yielded 0·75 g, the purified product destroyed the bacterial virus within 5 min in a dilution of 1:50,000, a concentration which allowed an abundant development of the coli organisms. The lowest concentration of acerin which exerted a slight colistatic effect was 1:200. Acerin was active only on the extracellular virus. A good antiviral effect on the virus host cell system was obtained in broth culture and even on solid media.

It was found that the active principle precipitated when increasing amounts of sodium chloride were added to the solution. Its virucidal effect was neutralized when it was exposed to serum diluted 1:2–32. In a concentration of 1:800 it also gave a precipitate with normal serum.

In discussing the possible chemical nature of the active principle in the acerin preparations, we were struck by the similarity in the properties of acerin to those of the vegetable tannins. The general occurrence of tannins in fruits and plant juices also contributed to our supposition that the active principle might be a tannin. It seemed tempting to ascribe the virucidal action of the acerin preparations to a tanning effect on the virus protein. The peculiar denaturation of the protein molecule caused by the tanning substances would provide a satisfactory explanation of the inactivation of the virus. Furthermore, the non-dialyzable tannins cannot reach the inside of the cell wall on the bacteria and would therefore act only on extracellular virus particles, as was the case with the acerin preparations. Moreover, the active principle could be precipitated with sodium chloride as can the tannins. Its neutralization in the presence of serum is also to be expected when serum proteins react with the tanning principle. As found by FISCHER, the strongest acerin preparation had a reddish-brown colour, in similarity to tannins, after treatment with alkali and subsequent oxidation in air. They also gave a greenish-brown precipitate with ferric chloride.

The virucidal effect of some vegetable tannins. It was found that several of the vegetable tannins exerted a virucidal action similar to that of the strongest acerin preparations. Eighteen natural tannins were analyzed[2]. In about the same concentration as the purest acerin preparations, 1:25,000, six of them, i.e., commercial tannic acid, Mimosa, ground Canaigre root, powdered Canaigre extract, Quebracho and Babul bark, killed the bacterial virus within 5 min.

Experimental. Both the pure tannic acid and the crude tannin preparations were dissolved in water. Any insoluble residue was removed and the solution dialyzed for 48 h at room temperature against distilled water, the outer liquid being exchanged several times. The content of the bags was then freeze-dried. The dry powder was analyzed for virucidal and bactericidal action as described earlier[3].

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[1] While this paper in print, our attention was called to a recent publication in J. Bact. (*66*, 572 1953) by CARSON and FRISCH about the growth inhibiting action of tannic acid on influenza virus *in ovo*. We were ignorant of this work and of the previous publication from 1948 by GREEN, Proc. Soc. Exptl. Biol. Med. *67*, 483 (1948).

[2] G. FISCHER, *Présence de substances antivirotiques dans différentes parties de plantes*, Ann. Pasteur No. 1480, *82*, 119 (1952).

[3] G. FISCHER, *A phagicidal and virucidal agent in maple fruit (acer platanoides L.) preparations–Investigations with E.Coli Bacteriophage and Vaccinia Virus*, Acta Pathol. Microbiol. Scand. *31*, 4 (1952).

[1] G. FISCHER, *Further investigations on the virucidal and antivirotic effect of a maple-fruit preparation-Acerin (Ac_{60}), performed with a coli culture and its bacterial virus*, Acta Pathol. Microbiol. Scand. No. *1381* (1954) (in Korrektur).

[2] We wish to express our thanks to Mr. K. H. GUSTAVSON, Doctor of Technology, of The Research Institute of the Swedish Tanning Industry, Stockholm, for his assistance and valuabel advice, as well as for his kindness in placing all the tannin preparations at our disposal.

[3] G. FISCHER, *A phagicidal and virucidal agent in maple fruit (acer plantanoides L.) preparations–Investigations with E. Coli Bacteriophage and Vaccinia Virus*, Acta Pathol. Microbiol. Scand. *31*, 4 (1952); *Further investigations on the virucidal and anti-virotic effect of a maple-fruit preparation-Acerin (Ac_{60}), performed with a coli culture and its bacterial virus*, Acta Pathol. Microbiol. Scand. No. *1381* (1954) (in Korrektur).