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NATIONAL ACADEMY OF SCIENCES

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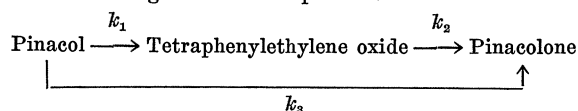
Washington University and St. Louis University, St. Louis, Missouri

Molecular Rearrangements of Aryl Pinacols and the Theory of Neighboring Group Displacement Reactions

Kenneth H. Adams and Herbert J. Gebhart, Jr.

St. Louis University

A kinetic study of the acid-catalyzed rearrangement of benzopinacol (tetraphenylethylene glycol) in acetic acid solution has shown that the pinacolone is formed by way of two simultaneous reactions. Approximately 80% of the pinacolone is formed by a reaction path that involves tetraphenylethylene oxide as an intermediate, whereas the remainder of the product is formed by a direct rearrangement of the pinacol:



The rate constants k_1 , k_2 , and k_3 have been evaluated.

From the point of view of neighboring group displacement theory, these results indicate that participation by C_β -hydroxyl is considerably greater than that by C_β -phenyl in this reaction. Whether this is due to a thermodynamically favored participation by C_β -hydroxyl or to the decreased participation of C_β -phenyl attributable to steric factors requires consideration. There is considerable evidence that the steric factor is important in these reactions.

Orthoquartzites in Missouri

Victor T. Allen and James T. Lift

St. Louis University

The LaMotte sandstone of Cambrian age, the Roubidoux, Everton, and St. Peter sandstones of Ordovician age, the Bushberg and Aux Vases sandstones of Mississippian age, and the Graydon sandstone of Pennsylvanian age in Missouri were studied petrographically.

According to Krynine's terminology, parts of these formations are orthoquartzites. The samples studied are of sedimentary origin, are composed of 95% or more quartz, and some have a silica cement. In much of these formations the silica cement is scanty or lacking and the sandstones are friable. Locally, the silica cement is absent, and carbonates, iron oxides, and clay are the cementing materials. The term "orthoquartzite" is unsatisfactory, because to some it indicates a well-indurated sandstone and to others a metamorphic rock. Long usage, as well as petrographic study, indicates that "quartzose sandstone" is a better term for these sedimentary rocks. Where desirable the nature of the cement can be indicated by the use of adjectives, such as silicinate and calcarinate; this was proposed in 1936 by the Subcommittee on Nomenclature of the Committee on Sedimentation of the National Research Council.

The Mathematical Development of the Formulas Essential to the Intelligent Use of Countercurrent Separations where the Number of Passes is Less than Twenty Five

Willard M. Allen

Washington University School of Medicine

Countercurrent distribution of several compounds between immiscible solvents has proved to be a very useful method of separating mixtures of both known and unknown compounds. These separations can be carried out either in a series of separatory funnels or in semiautomatic machines.

When the compounds in question have sufficiently different solubility constants, the number of distributions necessary to achieve virtually complete separation can be materially reduced by selecting the proper ratio of volumes of the upper and lower layers. Further, it is relatively easy to calculate the total amount of a given compound that is present in all the tubes from analysis of the amount present in either phase in tubes at or near the maximum.

The mathematical considerations necessary for the selection of the optimum ratio of the upper and lower layers, the calculation of the distribution constants, and the total amount of the compounds present are given.

The Ecology of Introggression in *Adenostoma*

Edgar Anderson, Washington University

Among variation patterns studied in various plant populations, one of the most curious was in *Adenostemma fasciculatum*, a component of the California chaparral, particularly in burned-over areas. It varied widely in inflorescence pattern from plant to plant, although it was frequently uniform in other characters. Analysis demonstrated that this variation was centered around (1) a low dense-flowered complex with short, wide leaves, and (2) a tall open-paniced complex with long, narrow leaves. The latter was found growing in the "Mother Lode" country. By extrapolation, a description of the other hypothetical parent was drawn up in such detail that it was identifiable as *Adenostemma fasciculatum* var. *obtusifolium*, native to islands and headlands in southern California. A re-examination of *Adenostemma* populations indicated them as varying widely between these two extremes, each of which contributes a character complex valuable in certain microhabitats of the chaparral but not in others. The low complex grows in thin soil under intense radiation but is not injured to long waterless periods. The tall complex can endure drought but has deep soil and less radiation. Each of these habitats (sea-coast and oak-savannah) is known to be geologically ancient, whereas the chaparral is comparatively recent. The combined evidence presents *Adenostemma* as a variable bicentered complex of hybrid origin, still highly plastic and

in a state of rapid evolutionary flux under the violent impact of man.

Recent Studies of Petrified Plants from the Central American Coal Fields

Henry N. Andrews, Jr., *Washington University*

During the past ten years petrified plants have been collected in some abundance from the Pennsylvanian age coal seams of the Central States, particularly Indiana, Illinois, Missouri, Iowa, and Kansas. These occur as calcified masses of plant remains, known as coal balls, which are found in the coal itself. At present they are known from numerous localities representing a wide stratigraphical range through the Pennsylvanian.

The fossils found in these petrifications include several groups of early seed plants, as well as abundant ferns and fern relatives. Our study of them has been undertaken chiefly to shed further light on the evolution of these groups and to trace connections with the more recent derivatives.

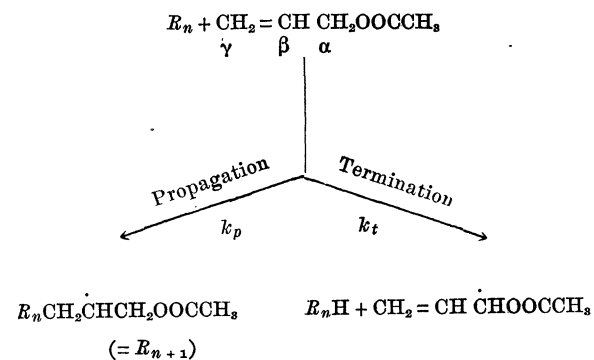
The study technique involves, first, rather extensive field exploration to obtain representative collections from as many different horizons as possible; these are prepared in the laboratory with the nitrocellulose peel method, the resultant sections being studied in essentially the same way that serial sections of a modern plant are dealt with.

These studies, now being carried on at several universities in the Midwest, have contributed notably to our knowledge of the seed ferns, the ferns, the lycopods, and articulates; we have also gained a much clearer understanding of the coenopterid ferns, a primitive group which appears to link the very primitive land plants of the Devonian with certain more advanced forms of the Carboniferous. These researches are, in general, in an early stage of development, and it seems likely that this source of information will, in the next few decades, contribute significant advances to our knowledge of plant morphology and evolution.

The Polymerization of α -Dideuteroallyl Acetate: Isotope Effects in Hydrogen Transfer

Paul D. Bartlett and Frederick A. Tate
Harvard University

It has been shown previously that in the polymerization of allyl acetate the chain-propagating and chain-terminating steps represent different modes of interaction between the same two molecular species:



Any change in the ratio $\frac{k_p}{k_t}$ between the rate constants for chain-propagation and chain-termination would be expected to affect both the average molecular weight of the polymer and the amount of polymer produced by a given amount of free-radical initiator.

Replacement of the α -hydrogen atoms of allyl acetate by deuterium indeed produces an increase of two- to threefold in these quantities. The results confirm the proposed mechanism of polymerization, since the termination reaction involves the transfer of hydrogen from one carbon atom to another and the propagation reaction does not.

There are indications in recent work that the magnitude of the isotope effect in hydrogen transfer reactions is a function of the electrical polarity assumed by the hydrogen during its transfer. These indications are discussed in terms of reaction rate theory.

Molecular Weight Determination by the Equilibrium Ultracentrifuge

J. W. Beams, A. Robeson, and N. Snidow
University of Virginia

Of the two general methods for determining molecular weights by the ultracentrifuge, the equilibrium method is the most reliable because it is based directly upon thermodynamic theory. The quantities measured in the equilibrium method during the centrifuging process are the rotor speed, the rotor temperature, and the concentration of the material under investigation across the centrifuge cell. In addition, the rotor speed and temperature must be held constant (or allowed to change slowly by a known amount) over a long period of time. The partial specific volume of the substance, which also must be known, is determined in separate experiments.

In the experiments here described the ultracentrifuge rotor is magnetically suspended in a vacuum and driven to the desired speed by an air turbine situated below the vacuum chamber. A thin, flexible shaft which passes through a vacuum gland connects the turbine and rotor. At operating speed the shaft is disconnected and the rotor coasts freely during the experiment, which usually extends over several days. The deceleration of the 7.5" diameter rotor is approximately 1 rps/day, and the rotor speed can be measured to one part in 10 million if so desired. The rotor temperature is held constant to within 0.01° C. The refractive index across the centrifuge cell, from which the concentration is found, is determined by a special interferometer method in which a fringe shift of less than 0.1 fringe can be measured. As a result, the precision is greater than in previous experiments and the observation can be extended to more dilute solutions.

The Limiting Thickness of an Electrolyzed Gas Film Capable of Sustaining a Given Negative Pressure

Lyman J. Briggs, *National Bureau of Standards*

The critical thickness of a gas film that is just capable of withstanding a given negative pressure P_N in a liquid column has been studied. The film was generated electrolytically on the surface of a spherical platinum electrode of known area. The number of gas molecules correspond-