A total of five preparations of *n*-octane from 2-octanone were made successfully, employing 2-ethylhexanol as solvent with sodium 2-ethylhexylate as catalyst and triethylene glycol with sodium methylate or sodium triethylene glycolate. The yields[12] of pure *n*-octane were consistently 65–68%, and the quantity of nitrogen evolved was nearly theoretical in each case.

Butylbenzene.[15]—The hydrazone was prepared in three hours from 148 g. (1.0 mole) of butyrophenone. It was decomposed at 170–210° in the usual manner, evolving 22 liters of nitrogen. The yield[12] was 66%; b. p. 180°; $n^{20}\mathrm{D}$ 1.4890.[16]

Cyclohexane.[15]—The hydrazone was prepared from 98 g. (1.0 mole) of cyclohexanone in one and one-half hours. A vigorous evolution of gas occurred at 203° during the Wolff–Kishner decomposition, which was complete in forty-five minutes. Yield of pure cyclohexane was 63%; b. p. 80.5°; $n^{20}\mathrm{D}$ 1.4261.[17]

***n*-Heptane.**[15]—A hydrazone was prepared from 114 g. (1.0 mole) of *n*-heptaldehyde in the usual manner. Gas evolution during the decomposition began at 108°, a lower temperature than experienced with any of the ketones. At 180°, the decomposition rate was very rapid, as evidenced by the nitrogen evolution rate. Yield of pure *n*-heptane was 54%; b. p. 98.0°; $n^{20}\mathrm{D}$ 1.3877.[18]

2,4-Dimethylheptane.[6,15]—Although diisopropyl ketone proved insoluble in triethylene glycol, the hydrazone preparation was made using 114 g. (1.0 mole) of ketone. Two layers were observed in the flask until a temperature of 110–120° was reached, at which point a vigorous reaction occurred with the formation of one liquid phase. The rest of the experiment proceeded smoothly except that only 10 liters of nitrogen were evolved in the decomposition. Two preparations were conducted in this manner, yielding only 16–17% of pure 2,4-dimethylheptane in each case.

Two further runs were made, using the modified procedure[6] and yields of 35–36% pure 2,4-dimethylheptane were realized: b. p. 78–80°; $n^{20}\mathrm{D}$ 1.3815.[19]

Ethylcyclopropane.[15]—A hydrazone was prepared from 84 g. (1.0 mole) of methyl cyclopropyl ketone in the usual manner. The decomposition was carried out after mixing the crude hydrazone and sodium methylate, yielding 57% of pure ethylcyclopropane. A second preparation, employing the modification whereby the hydrazone solution is added slowly to the hot alkali,[6] resulted in a 60% yield of ethylcyclopropane: b. p. 36.0°; $n^{20}\mathrm{D}$ 1.3784.[20]

Summary

The Wolff–Kishner reaction has been successfully employed in reducing one aldehyde and six ketones of various types to the corresponding low molecular weight hydrocarbons without any pressure equipment. Utilizing readily available solvents and catalysts, this reaction at atmospheric pressure was found to yield pure hydrocarbons in good yields and in reasonable time without any operation dangers. No evidence of rearrangement was noted.

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(15) Using 120 g. of 85% hydrazine hydrate, 440 ml. triethylene glycol and 6 ml. gl. acetic acid in preparation of the hydrazone. Sodium methylate (0.5 mole, 27 g.) was the decomposition catalyst. Refer to the General Procedure for details of operation.

(16) B. p. 182.1–183.1°; $n^{20}\mathrm{D}$ 1.4880: Evans, *J. Inst. Petroleum Tech.*, **24**, 537 (1938).

(17) B. p. 80.8°; $n^{20}\mathrm{D}$ 1.4262: Wibaut, *Rec. trav. chim.*, **58**, 329 (1939); **59**, 1220 (1940).

(18) B. p. 98.4°; $n^{20}\mathrm{D}$ 1.3877: Brooks, *J. Research Nat. Bur. Standards*, **24**, 44 (1940); see also ref. 17.

(19) B. p. 80.6°; $n^{20}\mathrm{D}$ 1.3815: Smittenberg, Hoog, Moerbeek and Zijden, *J. Inst. Petroleum Tech.*, **26**, 294 (1940); see also ref. 17.

(20) B. p. 35.8°; $n^{20}\mathrm{D}$ 1.3789: Lespieaux, *Bull. soc. chim.*, [4] **47**, 847 (1930).

STATE COLLEGE, PENNSYLVANIA RECEIVED JUNE 20, 1945

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Radical Chain Processes in Vinyl and Diene Reactions

BY HUGH S. TAYLOR AND ARTHUR V. TOBOLSKY

The polymerization of vinyl and diene derivatives occurs in many cases by a radical chain mechanism, the chain being initiated by addition of a free radical to the double bond of the substrate.

In addition to linear growth, various other important reactions occur both during the polymerization process and after the apparent completion of polymerization. These include branching, cross-linking, depolymerization or scission, cyclization and autoxidation of the long chain molecules. These competing reactions which we shall term subsidiary reactions, also are radical chain reactions, and it is the purpose of this paper to bring out the fundamental similarities in chemical mechanism underlying all of these apparently diverse phenomena.

The subsidiary reactions profoundly affect the physical properties of vinyl and diene plastics maintained at elevated temperatures, and these changes are collectively known as "aging." Oxygen and peroxides play a fundamental part in the natural or accelerated aging of these substances. Several new experimental techniques have been developed which allow a separation of the effects of these simultaneously occurring reactions and by means of these methods the kinetics of the reactions can be studied.

Polymerization.—The commonly accepted version of the nature of vinyl and diene polymerization was formulated through the efforts of Staudinger,[1] Mark,[2] Schulz[3] and many others. Also earlier work had established the possibility of polymerization of ethylene through the introduction of free radicals.[4,5] The most important processes occurring under the conditions of polymerization are chain initiation, chain growth and chain termination.

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(1) H. Staudinger, "Die Hochmolekularen organischen Verbindungen," Springer, Berlin, 1932.

(2) H. Dostal and H. Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

(3) G. V. Schulz and E. Husemann, *ibid.*, **B34**, 187 (1936); **B36**, 184 (1937); **B39**, 246 (1938).

(4) H. S. Taylor, *Proc. Am. Phil. Soc.*, **65**, 90 (1926).

(5) H. S. Taylor and W. H. Jones, THIS JOURNAL, **52**, 1111 (1930).

VINYL POLYMERIZATION

Initiation: $\mathrm{CH_2{=}CHX + R\cdot \longrightarrow CH_2RCHX\cdot}$

Growth: $\mathrm{CH_2RCHX\cdot + CH_2{=}CHX \longrightarrow CH_2RCHXCH_2CHX\cdot}$ etc.

Termination: by radical combination or disproportionation

DIENE POLYMERIZATION

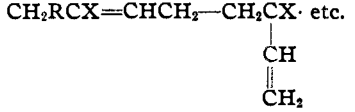
Initiation: $\mathrm{CH_2{=}CX{-}CH{=}CH_2 + R\cdot \longrightarrow CH_2R{-}CX{=}CHCH_2\cdot}$

Growth: 1,4 addition $\mathrm{CH_2RCX{=}CHCH_2\cdot + CH_2{=}CX{-}CH{=}CH_2 \longrightarrow}$

$\mathrm{CH_2RCX{=}CHCH_2CH_2CX{=}CH{-}CH_2\cdot}$

$\mathrm{CH_2RCX{=}CHCH_2CH_2CX{=}CH{-}CH_2\cdot}$

1,2 addition $\mathrm{CH_2RCX{=}CHCH_2\cdot + CH_2{=}CXCH{=}CH_2 \longrightarrow}$



$\mathrm{CH_2RCX{=}CHCH_2{-}CH_2\underset{\underset{\displaystyle CH_2}{\|}}{\underset{\displaystyle CH}{|}}{C}X\cdot}$ etc.

Termination: by radical combination or disproportionation.

Transfer Reactions.—In addition to the processes of initiation, growth, and termination, a process of chain transfer has also been proposed by Flory[6] to account for the experimentally observed facts in vinyl and diene polymerizations. This postulates that a growing chain may terminate by transferring its radical activity to an unactivated monomer which thereupon continues to grow by monomer additions. In addition to transfer to monomer, certain solvents and other materials used in the polymerization process may also act as transfer agents. The result of such a transfer is to reduce the average size of the polymerized product without altering the rate of polymerization as measured by monomer conversion.

The principle of microscopic reversibility would lead us to suspect that not only can a growing chain transfer its radical activity to a monomer or to some other inactive molecule, but that an active monomer or any free radical can transfer to an inactive long chain molecule. Furthermore, it appears quite reasonable to expect that the active radical can transfer its activity to any place along the chain rather than only at the chain end, and in this way secondary and tertiary radicals may be produced.[6]

Initial Step for Subsidiary Reactions.—The subsidiary reactions of the long chain molecules, namely, scission or depolymerization, branching and cross linking all involve the presence of an odd electron active center along the hydrocarbon chain. A very small amount of these active centers may possibly be always present in thermal equilibrium with the hydrocarbon, but probably the majority of these hydrocarbon radicals are formed by the action of oxygen or from free radicals persisting from polymerization.

$$\mathrm{{-}(CH_2CHX)_mCH_2CHX(CH_2CHX)_n{-} + O_2 \longrightarrow {-}(CH_2CHX)_mCH_2\dot{C}X(CH_2CHX)_n + \cdot OOH}$$

or

$$\mathrm{{-}(CH_2CHX)_mCH_2CHX(CH_2CHX)_n{-} + R\cdot \longrightarrow {-}(CH_2CHX)_mCH_2\dot{C}X(CH_2CHX)_n + RH}$$

$$\mathrm{{-}(CH_2CX{=}CHCH_2)_mCH_2CX{=}CHCH_2{-}(CH_2CX{=}CHCH_2)_n{-} + O_2 \longrightarrow {-}(CH_2CX{=}CHCH_2)_m\dot{C}HCX{=}CHCH_2(CH_2CX{=}CHCH_2)_n{-} + \cdot OOH}$$

or

$$\mathrm{{-}(CH_2CX{=}CHCH_2)_mCH_2CX{=}CHCH_2(CH_2CX{=}CHCH_2)_n{-} + R\cdot \longrightarrow {-}(CH_2CX{=}CHCH_2)_m\dot{C}HCX{=}CHCH_2{-}(CH_2CX{=}CHCH_2)_n{-} + RH}$$

In other words, oxygen or other free radicals can attack the hydrocarbon chain by abstracting a hydrogen atom. Previous investigation of radical attack on short chain hydrocarbons have indicated that the hydrogen atoms on tertiary carbons or on the methylene group alpha with respect to the double bond are most readily attacked.[7,8] The relative stability of the ·OOH fragment can be inferred from its role in the reaction between atomic hydrogen and oxygen[9] and from the fact that potassium suboxide, $\mathrm{KO_2}$, exists as a stable salt.[10] The susceptibility of the α methylene group in rubber to oxidative attack with the formation of the hydroperoxide group has been particularly emphasized by Farmer.[11]

The hydrocarbon radical thus produced can now undergo various secondary reactions.

Depolymerization.—The investigation of the self-disproportionation of hydrocarbon radicals has been extensively investigated with regard to the pyrolysis of short chain hydrocarbons. Theory and experiment are admirably presented by Rice and Rice,[12] who summarize the rules for self-disproportionation. Starting with the radicals already discussed and using these rules we obtain:

Depolymerization: Vinyl Polymers

$$\mathrm{{-}[CH_2CHX]_mCH_2\dot{C}X[CH_2CHX]_n{-} \longrightarrow {-}[CH_2CHX]_{m-1}CH_2CHX\cdot + CH_2{=}CX[CH_2CHX]_n{-}}$$

$$\mathrm{[CH_2CHX]_{m-1}CH_2CHX\cdot \longrightarrow [CH_2CHX]_{m-2}CH_2CHX\cdot + CH_2{=}CHX}$$

. . . .

Depolymerization: Diene Polymers

$$\mathrm{{-}[CH_2C(CH_3){=}CHCH_2]_m\dot{C}HC(CH_3){=}CHCH_2{-}[CH_2C(CH_3){=}CHCH_2]_n{-} \longrightarrow {-}[CH_2C(CH_3){=}CHCH_2]_mCH{=}C(CH_3)CH{=}CH_2 + \cdot[CH_2C(CH_3){=}CHCH_2]_n{-}}$$

$$\mathrm{{-}[CH_2CH{=}C(CH_3)CH_2]_{n-1}CH_2CH{=}C(CH_3)CH_2\cdot \longrightarrow {-}[CH_2CH{=}C(CH_3)CH_2]_{\cdot n-1} + CH_2{=}CHC(CH_3){=}CH_2}$$

It is clear that the reactions discussed above are straightforward depolymerizations, being actually the reverse of the polymerization process. According to these ideas a splitting can first occur at any place along the chain, followed by an unravelling of the chain by a continued splitting off of monomer units. Thus, depolymerization appears to be a chain reaction that may well involve

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[6] P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

[7] J. O. Smith, Jr., and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

[8] H. S. Taylor and J. O. Smith, Jr., *ibid.*, **8**, 543 (1940).

[9] H. S. Taylor and A. L. Marshall, *J. Phys. Chem.*, **29**, 1140 (1925); *Trans. Faraday Soc.*, **21**, 560 (1925).

[10] E. W. Neuman, *J. Chem. Phys.*, **2**, 31 (1934).

[11] E. H. Farmer, *Trans. Faraday Soc.*, **38**, 341, 348, 356 (1940).

[12] "The Aliphatic Free Radicals," by F. O. Rice and K. K. Rice, Johns Hopkins Press, Baltimore, Md., 1935.

a very large number of steps as compared to those found in the pyrolysis of short chain hydrocarbons. That such a reaction must occur is clear from the principle of microscopic reversibility. One can, in fact, estimate the energy of activation for this depolymerization as being equal to the energy of activation for chain growth plus the heat of reaction. Inasmuch as the energy of activation for propagation has been variously estimated as about 5 kcal. and the heats of polymerizations for vinyl and diene polymerizations are 20 kcal. (or less), it is clear that the heat of activation for depolymerization should be about 25 kcal. If the frequency factor for this reaction is normal, this relatively low activation energy would indicate a fairly rapid depolymerization even at temperatures that are not very high. Since of course this depolymerization competes with polymerization, we may expect that thermodynamic considerations may be of importance in determining the final distribution in molecular sizes under any given set of experimental conditions.

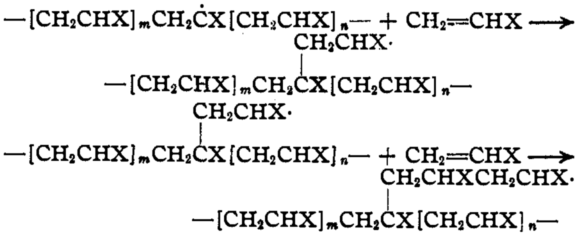
It is perhaps well to point out that scission agents which only cut long chains once and do not cause a splitting off of monomer would act in much the same way as transfer agents, namely, they would decrease the average polymer size without affecting the rate of monomer conversion during polymerization. On this basis it would be hard to distinguish between chain transfer agents and chain cutting agents.

A further application of the principle of entire equilibrium would lead us to predict that chain transfer may also play an important role in depolymerization because, since polymer radicals can transfer to monomer, the reverse reaction may also occur. In certain cases the activation of monomer to radicals takes place more readily than the activation of completed polymer and in these instances the presence of monomer and the possibility of radical transfer to polymer would enable depolymerization to proceed more rapidly than in the absence of monomer.

Evidence for the above statement has been obtained in experiments performed in conjunction with Mr. R. B. Mesrobian, and soon to be published, in which it has been shown that solutions of high molecular weight polystyrene in toluene are quite stable to heat and light (3000–6000 Å.) if oxygen is carefully excluded; however, under certain conditions replacement of a small portion of the high polymeric chains by an equivalent weight of monomer will cause first a slight increase and then a substantially larger decrease of the relative viscosity of the irradiated polystyrene solution even when air is carefully excluded. In fact the steady state viscosity finally attained in this case is the same as is reached by the monomer-free polystyrene solutions under the same conditions of light and heat in the case that oxygen is present. Apparently light in the wave length region used and in the absence of oxygen can activate only the unsaturated monomer, and the eventual degradation under the conditions described above is caused by transfer to the inactive polymer molecules.

Branching and Cross-linking.—In addition to self-disproportionation and the ensuing process of depolymerization, the hydrocarbon radicals can also react with monomer or with neighboring chains giving rise to branching and cross-linking, or may interact intramolecularly giving rise to cyclization.

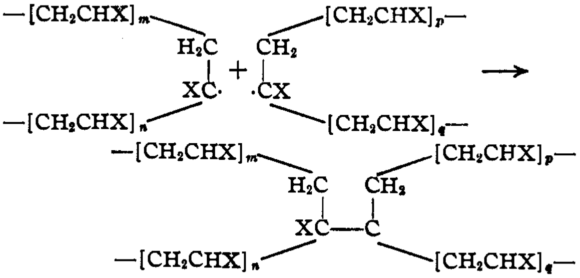
The branching process for vinyl polymers can be represented as follows



$$-[CH_2CHX]_mCH_2\dot{C}X[CH_2CHX]_n- + CH_2{=}CHX \longrightarrow -[CH_2CHX]_mCH_2\overset{\displaystyle CH_2CHX\cdot}{\overset{|}{C}}X[CH_2CHX]_n-$$

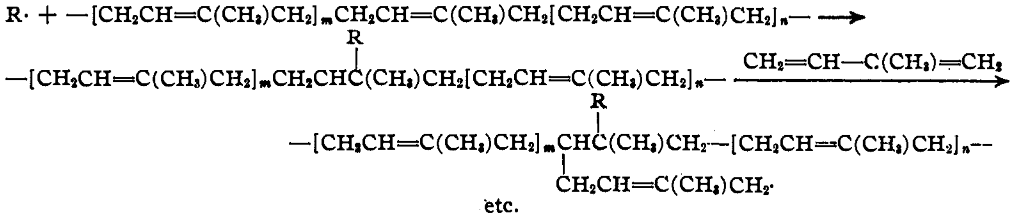
$$-[CH_2CHX]_mCH_2\overset{\displaystyle CH_2CHX\cdot}{\overset{|}{C}}X[CH_2CHX]_n- + CH_2{=}CHX \longrightarrow -[CH_2CHX]_mCH_2\overset{\displaystyle CH_2CHXCH_2CHX\cdot}{\overset{|}{C}}X[CH_2CHX]_n-$$

Cross-linking in vinyl polymers occurs when two radicals combine in the following manner



This process of radical recombination is naturally a fairly uncommon one.

In the case of diene polymers trifunctional branching can occur exactly as in the case of vinyl polymers or it can also occur during or after polymerization due to the action of free radicals from catalyst fragments or other free radicals as follows



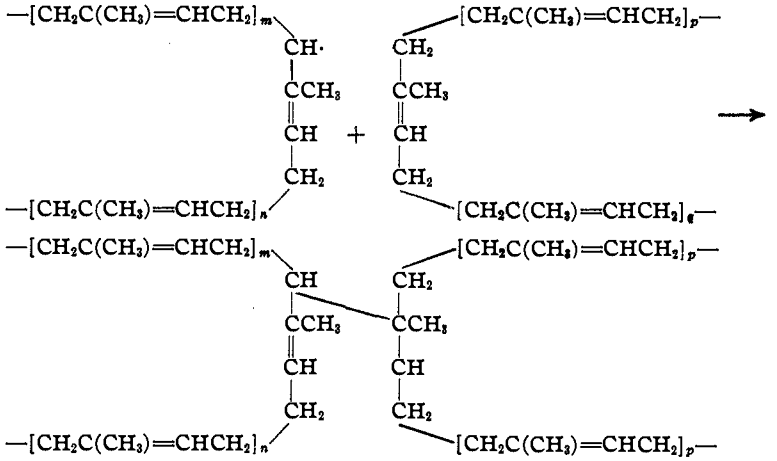
$$R\cdot + -[CH_2CH{=}C(CH_3)CH_2]_mCH_2CH{=}C(CH_3)CH_2[CH_2CH{=}C(CH_3)CH_2]_n- \longrightarrow$$

$$-[CH_2CH{=}C(CH_3)CH_2]_mCH_2CH\overset{\displaystyle R}{\overset{|}{C}}(CH_3)CH_2[CH_2CH{=}C(CH_3)CH_2]_n- \xrightarrow{CH_2{=}CH-C(CH_3){=}CH_2}$$

$$-[CH_2CH{=}C(CH_3)CH_2]_m\underset{\displaystyle CH_2CH{=}C(CH_3)CH_2\cdot}{\underset{|}{CH}}\overset{\displaystyle R}{\overset{|}{C}}(CH_3)CH_2-[CH_2CH{=}C(CH_3)CH_2]_n-$$

etc.

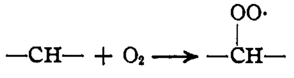
Cross-linking can also occur much more readily in diene polymers than in vinyl polymers because, in the former case, a radical hydrocarbon can add to a double bond in a neighboring chain



Role of Oxygen.—The peculiar role of oxygen in vinyl polymerizations where it acts both as catalyst and as inhibitor has been recently discussed.[13] In small concentrations oxygen is in many cases necessary because it forms peroxides which initiate radical chains. In large concentrations oxygen reacts with already formed radicals (which may be formed from any or all sources such as the action of ultraviolet light) to give superoxides, this reaction competing favorably with the growth or polymerization reaction.

So far as the action of oxygen on already completed diene or vinyl polymers is concerned, Farmer[14] has postulated that the initial reaction in the oxidation of rubber is the formation of a hydroperoxide on the methylene group alpha to the double bond which can then undergo various secondary reactions including attack on the double bond to form cyclic ethers, peroxidic chain scission yielding alcoholic, aldehydic or carboxylic groups and peroxidic cross-linking. The presence of the hydroperoxide groups during oxidation has been chemically established. It should be pointed out, however, that the hydroperoxide group may well be formed in part by radical recombination of hydrocarbon radical with the OOH fragment. According to the viewpoint adopted here the chemical combinations of vinyl and diene polymers with oxygen which undoubtedly occur during aging should be chiefly regarded as the result of secondary reactions. The fundamental role of oxygen is to produce and maintain a supply of hydrocarbon free radicals, the reactions of which (scission and cross-linking) produce the important changes in physical properties. Oxygen, therefore, acts chiefly as a catalyst, but is chemically combined with the polymer in the process. Farmer apparently ascribes a more direct role to the oxygen molecule through the agency of the hydroperoxide group. It seems difficult at present to make a clear-cut decision between these somewhat complementary viewpoints and, in fact, Farmer suggests, though less explicitly, many of the mechanisms discussed here.

Role of Oxygen in Promoting Branched Radical Chains.—Oxygen is known to add to free radicals and one of its most important roles (which would also highlight the role of the hydroperoxide group) may be the production of branched kinetic chains of the following type[11,15]:



$$-\text{CH}- + \text{O}_2 \longrightarrow -\overset{\text{OO}\cdot}{\overset{|}{\text{CH}}}-$$

$$-\text{HC(OO)}\cdot- + -\text{CH}_2- \longrightarrow \text{HC(OOH)} + -\text{HC}-$$

$$-\text{HC(OOH)}- \longrightarrow -\text{HC(OO)}\cdot- + \text{H}\cdot$$

or

$$-\text{HC(OOH)}- \longrightarrow -\text{HC}- + \cdot\text{OOH}$$

The hydrocarbon radicals produced in this branched chain process may then undergo the various reactions of depolymerization, branching and cross-linking previously described.

Isolation of the Subsidiary Reactions.—One of the most striking facts concerning the degradative processes of scission and cross-linking (or branching) of diene and vinyl polymers is the simultaneous occurrence of these reactions with nearly equivalent rates over practically the entire temperature range. This apparently means that the activation step for these reactions is the same and in this article we have postulated that in every case a hydrocarbon free radical is the activated state. The molecules containing the radical can either split or link with another molecule (or with itself causing cyclization) and the relative rate with which these processes will occur will depend on the nature of the polymer and upon the proximity of groups like double bonds suitable for radical attack. The radicals can also add oxygen as above.

It is possible largely to suppress the cross-linking reaction without markedly changing the rate of scission by dissolving the vinyl or diene polymer in dilute solution. The rate of chain scission, not complicated by the cross-linking reaction, can be followed by measuring the rate of decrease of viscosity with time of heating under various conditions of temperature, oxygen concentration, catalytic environment and so on. Swelling by organic solvents of three dimensional structures such as vulcanized rubbers also keeps the molecular chains apart and thus slows down the rate of cross-linking without seriously affecting the rate of scission. It is, therefore, possible to disperse such three-dimensional structures in suitable

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(13) C. E. Barnes, This Journal, 67, 217 (1945).

(14) E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 125 (1943).

(15) Emphasized by Dr. H. M. Spurlin in a private discussion with the junior author.

swelling agents by heating at elevated temperatures even though in the unswollen condition certain of these materials may tend to harden because the rate of cross-linking may be more rapid when the molecules are close together than the rate of scission.

The measurement of relaxation of stress at constant extension isolates and measures only the scission reaction since the cross linking which is occurring simultaneously takes place in such a way as not to affect the stress in samples maintained at constant elongation (to a first approximation).[16,17] On the other hand, intermittent measurements of modulus, with the sample kept in a relaxed state between modulus determinations measure the sum of cross-linking and scission reactions. Measurements of this kind on vulcanizates of natural rubber and various synthetic rubbers demonstrate that scission and cross-linking are occurring at comparable rates in all rubbers and confirm the very important role of oxygen in these processes.[16,17] Recent experiments proving the simultaneous existence of polymerization and degradation in toluene solutions of styrene and polystyrene also appear to fit into the general kinetic picture developed here.[18]

Summary

A general mechanism for various reactions of vinyl and diene polymers is presented which emphasizes the role of the hydrocarbon free radical as the activated state which can undergo various competing subsidiary reactions that profoundly affect the physical properties of these materials.

The mechanism further emphasizes the chain characteristics of depolymerization processes, occurring by reversal of the steps in the chain growth processes, at velocities which are significant even at moderate temperatures owing to the small activation energies involved.

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[16] A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. Applied Phys.* (*U. S. S. R.*), **15**, 380 (1944).

[17] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945).

[18] R. B. Mesrobian and A. V. Tobolsky, THIS JOURNAL, **67**, 785 (1945).

PRINCETON, N. J. RECEIVED JULY 21, 1945

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics and Mechanism of the Isomerization of Cyclopropane

BY E. S. CORNER[1] AND R. N. PEASE

During recent years there has been a divided opinion on the status of the quasi-unimolecular reaction. Formerly the Hinshelwood–Lindemann theory[2] was almost universally accepted as providing the explanation for the breakdown of first order constants at low pressures. However, many of these reactions on further examination proved to be far more complex than demanded by the simple theory. The existence of free radicals in the reaction mixture was established in many cases, thus indicating a chain rather than a unimolecular mechanism.

The radical-chain theory, developed by F. O. Rice,[3] allows for greater latitude in the kinetic expression, depending upon the type of chain mechanism adopted. The available data occasionally may be equally well fitted to either a quasi-unimolecular or a 1.5 order rate law, permitting no clear decision. In fact, it has been questioned whether any reaction offers confirmatory evidence of the quasi-unimolecular type, with the possible exception of certain isomerization reactions.[4] These appear to be free of complicating side reactions and a chain mechanism has seemed improbable.

Among such reactions, the isomerization of cyclopropane to propylene is of special interest. Preliminary measurements by Trautz and Winkler[5] indicated that the reaction is first-order and homogeneous. Subsequent investigation by Chambers and Kistiakowsky[6] revealed that first-order constants fell by about 45% between 700 and 10 mm. initial pressure (500°), although maintaining reasonable constancy with increased conversion at any one pressure. Formal classification as a quasi-unimolecular type was thus strongly indicated, and data were successfully treated on this basis.

Although this evidence appeared fairly conclusive, there remained the question of the effects of added gases. In addition, the method of analysis employed by Chambers and Kistiakowsky is open to question, since it involved determination of propylene by absorption in 3% potassium permanganate solution and calculation of cyclopropane by difference. Results would be vitiated if propylene polymerized or decomposed. For these and other reasons, we have re-investigated the reaction.

Experimental

Apparatus.—The reaction was studied in a static system of conventional design, consisting of a 200-cc. clean Pyrex reaction bulb, manometer and storage bulbs. The system was evacuated by means of a mercury diffusion pump.

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[1] Present address: Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey.

[2] Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press, New York, N. Y., 1940, p. 78 *et seq.*

[3] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

[4] Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, N. J., 1942, p. 122 *et seq.*

[5] Trautz and Winkler, *J. prakt. Chem.*, **104**, 53 (1922).

[6] Chambers and Kistiakowsky, THIS JOURNAL, **56**, 399 (1934).