mixtures of oxalic and benzene carboxylic acids had shown that the former can be titrated quantitatively in the presence of the latter.

Decarboxylation.—Previous work with the oxidation products of coal had indicated the difficulty of recovering in good yields the individual pure aromatic acids present, so recourse was had to decarboxylation as a method of establishing aromatic character.[6] In some cases the solutions remaining, after the aliquots had been removed for analytical work, were concentrated until salts began to separate and placed in the middle compartment of a three-compartment cell, subjected to electrolysis, and the free acids recovered by vacuum evaporation of the anode liquors on the water-bath. The required amount of alkali was added and the decarboxylation carried out as previously described.[9] In other cases the alkali salts were evaporated to a small volume and decarboxylated directly.

Summary

The presence of C_6 ring structures in products obtained by pyrolyzing cellulose at temperatures up to 400° has been established by oxidation followed by decarboxylation and recovery of benzene and diphenyl. The yield of aromatic hydrocarbons, based on the pyrolyzed cellulose, is of the same order as that obtained by similar attack on a Pittsburgh seam bituminous coal. It has been pointed out that the presence of C_6 ring structure in bituminous coal does not exclude the possibility of such coals having been derived from cellulose.

PITTSBURGH, PENNA. RECEIVED DECEMBER 2, 1936

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[9] Ref. 6, page 2326.

[CONTRIBUTION NO. 47 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Oxidation of a Pittsburgh Seam Bituminous Coal and Low Temperature Coke by Alkaline Permanganate

BY B. JUETTNER, R. C. SMITH AND H. C. HOWARD

The present generally accepted picture of the structure of bituminous coal as a system containing condensed rings is based largely on evidence from oxidation experiments.[1] Certain bituminous coals have been reported to yield as much as 46% of their carbon as benzene carboxylic acids on oxidation with alkaline permanganate.[2] Obviously such high yields of one type of compound are of great theoretical interest, and are of possible technical importance.

A study has been made of the nature of the products obtained by exhaustive alkaline permanganate oxidation of a Pittsburgh seam coal[3] and a 500° coke prepared from this coal. It has been found that 90–95% of the carbon of these materials can be recovered after oxidation as a solution of water soluble, non-colloidal acidic products, which vary in color from pale yellow to deep reddish-brown, depending upon the amount of permanganate employed and the oxidation period. Typical data showing the distribution of the carbon[4] among the chief oxidation products are given in Table I. The assumption that the carbon not found as carbonic, oxalic and acetic acids is in aromatic acids, is based upon the fact that the only condensable hydrocarbons recovered by decarboxylation were aromatic and consisted chiefly of benzene and diphenyl. On this basis it is evident that a significant fraction of the carbon in the Pittsburgh coal is in cyclic structures and that coking increases the proportion of cyclic carbon present. However, we have found no evidence that would justify a statement that any considerable fraction of the acids produced by the action of alkaline permanganate on this coal consists of benzene carboxylic acids.

TABLE I

CARBON DISTRIBUTION IN POTASSIUM SALTS

Material		Edenborn coal	500° Edenborn coke
Carbon as	Carbonic acid, %	45.0	40.7
	Acetic acid, %	2.2	1.6
	Oxalic acid, %	15.0	11.6
	Arom. acids (diff.), %	30.8	37.1
Total C recov. as K salts, %		93.0	91.0

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[1] For a review of the work of F. Fischer and co-workers, see Horn, *Brennstoff-Chem.*, **10**, 362 (1929); Bone and co-workers, *Proc. Roy. Soc.* (London), **A110**, 537–542 (1926); **A127**, 480–510 (1930); **A148**, 492–522 (1935). Recent hydrogenation work by Biggs, THIS JOURNAL, **58**, 1020 (1936), constitutes even more convincing evidence.

[2] Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935).

[3] Described in detail in Bur. Mines Tech. Paper 525, 1932.

[4] The general procedure described in ref. 2 has been used. These authors do not reveal the method employed to determine the carbon reported as oxalic and benzene carboxylic acids in their carbon balances.

Recovery and Identification of Acids.—The recovery in good yields of the free acids from their potassium salts presented great difficulties, since all are readily soluble in water and have unfavorable distribution coefficients in solvent systems such as water and ether. The procedure described by Bone, Horton and Ward,[5] the addition of the theoretical amount of sulfuric acid, followed by evaporation to dryness and extraction of the dried residue with ether and acetone, gave poor recoveries and, indeed, on theoretical grounds it is difficult to see why complete metathesis to free acids and potassium sulfate should take place. Two methods have been developed which give satisfactory recoveries of the free acids. They are: (1) acidification of the solution of potassium salts with sulfuric acid followed by extraction of the solution with ether in a continuous extractor of the type described by Kester,[6] and (2) decomposition of the salts by electrolysis in a three-compartment cell. The recoveries of acids obtained by the two methods are illustrated in Table II. The data show that the recovery of the higher molecular weight acids is more complete by electrolysis than by extraction. In confirmation of this it has been observed that while the central compartment in the electrolytic cell ultimately becomes colorless, even very prolonged extraction fails to remove all the color from the aqueous layer in the extraction process. Secondary oxidation of the aromatic acids at the anode during electrolysis appears to be inconsiderable. Because of the high recoveries and the simplicity and convenience of the method, the separation by electrolysis has been used almost exclusively.

TABLE II

COMPARISON OF METHODS OF RECOVERY OF ACIDS

Material	K salts	Acids recov. by elect.	Acids recov. by 78-hr. ether extn.
Carbon as:			
Total, g.	100	45.5	40.7
Carbonic acid, g.	48.5		
Acetic acid, g.	2.3		
Oxalic acid, g.	15.9	13.7 86%	15.6 98%
Arom. acids (diff.), g.	33.3	31.8 96%	25.1 72%

The anode liquors containing the free acids were concentrated in vacuum on the water-bath, but it was found necessary to conduct the final drying operation at not over 50° to prevent discoloration. The acids so recovered are yellow to light buff in color, almost free from inorganic impurities, and completely soluble in water, alcohol and ethyl ether. Since they have all migrated through parchment, the color cannot be due to colloidal or high molecular weight impurities. They contain 30–40% oxalic acid; the carbonic and volatile organic acids are, of course, not recovered. The average yield from Edenborn coal has been 88 g. of these mixed acids per 100 g. of coal; the yield from the coke is higher, 98 g. per 100 g.

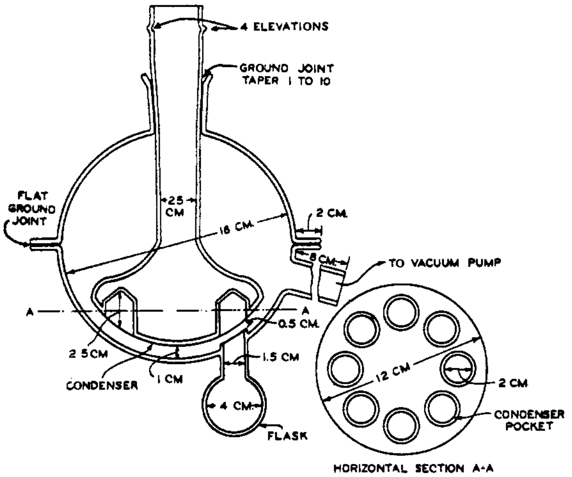

Fig. 1.

The first attempt to isolate pure compounds from the mixed acids was by esterification with diazomethane followed by fractionation in a high vacuum still, Fig. 1. Typical data from such a fractionation are shown in Table III. A significant part of these esters was not distillable even at 300° in a vacuum of 1 micron. From the low boiling fractions considerable amounts of crystalline dimethyl oxalate separated; higher fractions ranged from limpid oils to semi-solid resinous products, and in no case was any pure crystalline material other than dimethyl oxalate recovered. The non-distillable residue was a reddish-brown, brittle resin.

The next attempts at separation were by means of the formation of characteristic salts. By saturation of an aqueous solution of the mixed salts with ammonia at low temperature a copious crystalline precipitate resulted. Mellitic acid precipitates almost quantitatively under these conditions, as a hydrated ammonium mellitate, and a considerable amount of the oxalic acid also separates as the monohydrated ammonium salt. The free acids from the insoluble ammonium salts

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(5) Bone, Horton and Ward, *Proc. Roy. Soc.* (London), **A127**, 489 (1930).

(6) Kester, *Ind. Eng. Chem.*, **24**, 1121 (1932).

TABLE III

FRACTIONATION OF METHYL ESTERS FROM COAL

(10.9 g. used)

Bath temp., °C.	Time to constant temp., min.	Time at constant temp., min.	Max. press., microns	Weight of condensate, g.	Nature of condensate
-120	60	75	5.5	1.60	White, crystalline
120–170	25	95	4.9	1.19	Colorless, glassy
170–220	25	95	2.6	2.20	Yellow, glassy, some crystals
220–300	25	60	9.1	0.44	Brown, resinous
		Condenser washings		1.13	
		Total distillate		6.56 g. = 60.2%	

TABLE IV

SEPARATION OF ACIDS AND FRACTIONATION OF ESTERS FROM COAL

(60.0 g. Acids Used)

	Acids recovered, g.	Esters, g.	Distillate up to 220° g.	Distillate up to 220° %	Methyl esters isolated g.	Methyl esters isolated g. per 100 g. coal
Insoluble ammonium salts	17.5[a]	14.1	11.3	80.0	6.0 oxalic	8.8
					0.4 mellitic[b]	0.6
Insoluble calcium salts	3.7[a]	1.8	0.45	25.0	.05 terephthalic	.08
Barium salts:						
A—Water insoluble						
(a) Insol. in acetic acid	10.2	12.5	3.46	27.7	.52 pentacarboxylic	.76
(b) Sol. in acetic acid	10.6	12.6	6.34	50.0	.46 prehnitic (?)	.67
					.05 pentacarboxylic	.07
B—Water soluble	11.0	13.4	7.15[c]	53.3		
Total	53.0 (88.3%)	54.4	28.7	52.8	7.48	11.0

[a] Large amounts of oxalic acid present, the ester of which is volatile, hence the yield of ester is poor. [b] From the residue, non-volatile at 220°. [c] Liquid at room temperature; no individuals isolated.

were recovered by electrolysis, esterified and distilled. No difficulty was encountered in isolating the pure hexamethyl ester of mellitic acid. The yield of pure ester from the coal was 0.6 g. per 100 g. of coal; from the coke, 0.8 g.

The soluble ammonium salts in the filtrate from the ammonia precipitation were converted to barium salts by excess barium hydroxide and these fractionated into water insoluble and soluble, and the water insoluble barium salts were separated again into two fractions, insoluble and soluble in glacial acetic acid. In the first two experiments separation into an insoluble calcium salt fraction was also made, but this proved of little value and was omitted in later work. The amounts of acids recovered from the different salt fractions, yields of total esters, and pure esters isolated are shown in Table IV. Work with an authentic sample of the methyl ester of benzene pentacarboxylic acid had shown that this ester distilled rapidly in our still at 220° at 1 micron pressure. It had also been observed in the earlier experiments with the esters of acids from coal that temperatures above 220° resulted in little increase in condensate, but considerable thermal decomposition. Accordingly in all later fractionations the maximum temperature used was 220°.

The relatively small proportion of the methyl esters from the coal acids distilling in the range in which authentic samples of the esters of the higher benzene carboxylic acids were known to distil rapidly, led to the conclusion that oxidation had been incomplete. Hence a sample of acids prepared by the oxidation of coke was re-oxidized with further amounts of alkaline permanganate for a two-week period. The permanganate used in the first oxidation was 8.9 g. per g. of coke; in the reoxidation an additional 1.4 g. was necessary. The distribution of the carbon before and after this reoxidation is shown in Table V. It is evident that under these conditions the aromatic acids are attacked. As a result of the further oxidation, the color of the acids in aqueous solution changed from reddish-brown to golden-yellow. There is also definite indication of oxidation of oxalic acid.[7]

Recovery of the acids, fractionation of the acids by salt precipitation and fractionation of

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[7] Bone and co-workers (ref. 2) reported that oxalic acid was not further oxidized by alkaline permanganate.

TABLE V

REOXIDATION OF ACIDS FROM COKE

Material	Orig. acids (22.8 g. oxalic 57.2 g. aromatic)	Reox. acids[a]
Carbon as:		
Carbonic acid, g.		10.47
Acetic acid, g.		0.11
Oxalic acid, g.	6.1	3.38
Arom. acids (diff.), g.	28.0	18.79
Total carbon, g.	34.1	32.75

[a] The reoxidized acids recovered by electrolysis weighed 55.5 g. and contained 12.6 g. oxalic and 42.9 g. aromatic acids.

the esters were carried out substantially as described for the products from coal. The data are collected in Table VI. As was found with the coal, a large fraction of these esters was not distillable at 220° and 1 micron pressure, and the same type of reddish-brown, resinous residue remained in the still. However, significantly greater amounts of hexamethyl mellitate and of the ester of the pentacarboxylic acid were isolated.

TABLE VI

SEPARATION OF ACIDS AND FRACTIONATION OF ESTERS

(50 g. of Reoxidized Coke Acids Used)

	Acids recov., g.	Esters, g.	Distillate up to 220° g.	Distillate up to 220° %	Distillable esters: Wt. of fractions and compounds isolated, g. –120°	120–170°	170–220°	Washings[a]	Non-vol. residue
Insol. ammonium salts	8.8	10.1	3.13	31	2.77[b]	0.01	0.07	0.28	4.13[f]
Barium salts									
A. Water insoluble									
(1) Insol. in acetic acid	26.8	32.8	16.5	50.4	2.52[b]	6.74[c]	4.21[e]	3.02	13.97
(2) Soluble in acetic acid	2.8	2.8	1.59	57.0	0.70[b]	0.48[d]	0.27[e]	0.15	0.48
B. Water soluble	3.6	Not esterified							
Total	42.0 (84%)								

[a] From the condenser. [b] Almost pure oxalate. [c] Mixed crystals; no individuals isolated. [d] Prehnitate from this fraction. [e] Pentacarboxylate from this fraction; 1.66 g. per 100 g. coke. [f] Mellitate from this fraction; 1.78 g. per 100 g. coke.

Because of the small amounts of definite compounds isolated by the methods described, we were led to the use of a more general means of characterizing these acids. It has been pointed out[8] that decarboxylation to the nuclear hydrocarbons constitutes such a tool, and that method was applied. The average yield of steam volatile hydrocarbons recovered by decarboxylation of the acids from coal was 7.7 g. per 100 g. coal, and from the coke acids, 11 g. The higher yield of aromatic hydrocarbons from the coke is in accord with the previously expressed view that carbonization results in increased condensation to cyclic structures. Fractionation of the hydrocarbons obtained by decarboxylation showed 50–60% to be benzene, identified by boiling point and refractive index; 10–15% boiled between 82 and 150° and was not identified; and from the high boiling residue diphenyl was recovered, in some cases amounting to 20% of the total hydrocarbons. Some diphenyl was always formed in decarboxylation experiments with known benzene carboxylic acids, but usually in small amounts, less than 5% of the total steam volatile hydrocarbons.

There appears little doubt that a significant fraction, 50–60%, of the non-volatile acids formed by alkaline permanganate oxidation of this coal and a 500° coke is aromatic. We have, however, found no evidence that any considerable amount of simple benzenoid acids is present. The persistent color and the failure of a large part of the esters to distil under conditions where the esters of authentic samples of benzene carboxylic acids evaporate rapidly, indicate that we are dealing with acids of more complex structure. Although all attempts to isolate them by specific reactions have failed, it seems probable that ketonic aromatic acids are present. Diphenyl was always recovered from the decarboxylation experiments on the acids from coal in significantly greater amounts than obtained in the work with known benzene carboxylic acids. Failure to isolate hydrocarbons more complex than diphenyl, by heating the acids with alkali to elevated temperatures, is not necessarily decisive evidence for the absence of acids with condensed aromatic nuclei, since the drastic alkali treatment may have resulted in scission of the nuclei of ketonic acids. Bamberger and Hooker[9] showed that a diphenyl carboxylic acid, and ultimately diphenyl, resulted

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[8] Juettner, Smith and Howard, THIS JOURNAL, **57**, 2324, 2326 (1935).

[9] Bamberger and Hooker, *Ann.*, **229**, 102–162 (1885).

from the fusion of a fluorenone carboxylic acid with alkali.[10]

Experimental

Oxidation.—Five hundred grams of the 200 mesh coal or coke[11] was suspended in about 35 liters of approximately 0.4 *N* potassium hydroxide solution, contained in an iron kettle which was provided with good mechanical agitation and heated by a large ring burner. The solid permanganate was added in small amounts over a period of several hours and such an excess used that about twelve hours of boiling was required for the discharge of the color. Under these conditions the coal consumed significantly greater amounts of permanganate than the coke; 11 g. per g. was used for the former and 8.9 for the latter. The ratio of grams of alkali per gram of coal or coke was 1.6.

The precipitated manganese dioxide was filtered off by suction on a 32-cm. Büchner funnel, thoroughly pressed, then returned to the kettle and agitated with a few liters of water. This operation was repeated three times. The combined filtrate and washings, approximately 50 liters, were concentrated until salts began to separate, diluted and then transferred to a volumetric flask of suitable size, 6500 cc. Aliquot portions of this solution were used for carbon balances and for the preparation of the free acids.

Carbon Balances.—Total carbon was determined by oxidation of a suitable sized aliquot, with chromic and sulfuric acids; carbonate carbon, by evolution with hydrochloric acid; volatile acids, by steam distillation, after acidification with dilute sulfuric acid, followed by titration of the distillate with standard alkali using phenolphthalein. Volatile acids were calculated as acetic. Oxalate carbon was determined by precipitation of the calcium salt with calcium acetate from an aliquot which was first acidified with hydrochloric acid, then made alkaline with potassium hydroxide, and finally acidified with glacial acetic acid. The calcium salt so obtained was never pure white in color and, on solution in dilute sulfuric acid and titration with standard permanganate, a much less stable end-point was obtained than with pure calcium oxalate. For this reason it is possible that the figures for oxalate carbon are high. The error is not thought to be appreciable. Experiments with mixtures of oxalic and authentic samples of benzene carboxylic acids showed that the former can be determined quantitatively, in the presence of the latter, by titration in acid solution with standard permanganate.

The difference between total carbon by oxidation with chromic and sulfuric acids, and the sum of the carbon found as carbonate, acetate and oxalate is reported as aromatic.

Recovery of Free Acids.—A suitable amount, 1000 cc., of the solution of potassium salts was placed in the middle compartment of a three compartment cell, such as is used for the purification of colloidal material by electrodialysis,[12] and electrolyzed between an anodic diaphragm of parchment and a cathodic diaphragm of cellophane, using a platinum gauze anode and a copper cathode, until the salts were completely decomposed. The acids were recovered by evaporation of the anode solutions in vacuum on the water-bath and the cathodic solutions, containing the potassium hydroxide formed by decomposition of the salts, were discarded. Anode and cathode compartments were emptied approximately twice every twenty-four hours and fresh distilled water added. At the close of the electrolysis the solution in the middle compartment was colorless and evaporation to dryness showed no significant amounts of inorganic or organic substances. In some cases the cathode liquors were pale yellow, indicating migration or diffusion of organic substances toward the negative electrode. The data of Table II show that the recovery of aromatic carbon is satisfactory.

The acids so recovered were relatively free from inorganic impurities; the residue on ignition was less than 1%. In the dry state they darkened and showed evidence of charring at temperatures as low as 100°; hence while the initial concentration was carried out on the water-bath, the final drying was at 50°. The anhydrous acids so prepared were yellow or tan in color, highly hygroscopic, very soluble in water, and soluble in ethyl ether. Analysis for oxalic acid by the method described showed it to be present in different preparations in amounts varying from 25–35%.

Esterification.—An appropriate amount, 20–40 g., of the mixed anhydrous acids, prepared as above, was dissolved in methyl alcohol or ether and subjected to exhaustive methylation, with diazomethane, by the method of Staudinger and Kupfer.[13] After the methylation the solvent was allowed to evaporate at room temperature and the yellow to reddish-brown sirupy mixture of esters was transferred to the molecular still for fractionation. The addition of silver powder to the sirupy mixture was found to facilitate its transfer to the still and eliminated spattering in the subsequent distillation A considerable part of the dimethyl oxalate was no doubt lost with the ether. After distillation the various ester fractions were removed mechanically as completely as possible from the pockets of the condenser. Any material still adhering to the condenser was removed by washing with acetone, and the amounts so recovered are shown in Table VI. The non-volatile residue was separated from the silver powder by extraction with acetone. Total recoveries were usually above 90%, except in those cases where dimethyl oxalate was present in large amounts. The various ester fractions were crystallized from acetone and water mixtures and the identity of the pure esters established by analysis and mixed melting point with authentic samples, except in the case of the ester of prehnitic acid. None of this acid or its ester was available.

Decarboxylation.—This was carried out as described elsewhere[8] (p. 2326).

Summary

The exhaustive oxidation with alkaline permanganate of a Pittsburgh seam bituminous coal, Edenborn mine, and of a 500° coke from this coal has been studied. It is shown that 90–95% of the carbon can be recovered as the potassium salts of water soluble, non-colloidal acids. Ap-

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[10] Recently Allen and L. Gilman, This Journal, 58, 939 (1936), have split diphenylnaphthacenequinone into benzoic and a diphenylnaphthacene carboxylic acid by alkali fusion.

[11] Prepared in a large rotating Fischer retort, heating rate 1.9° per minute; held at 500° for one hour.

[12] A ceramic cell, supplied by Maurice A. Knight, Akron, Ohio, and constructed according to the design of Bradfield, was employed.

[13] Staudinger and Kupfer, *Ber.*, **45**, 505 (1912).

proximately 30 and 35% of the carbon of the coal and coke, respectively, is found as aromatic acids.

It has been shown that good recoveries of oxalic and aromatic acids can be obtained by direct electrolytic decomposition, in a three compartment cell, of the potassium salts resulting from the oxidation. Oxalic plus aromatic acids recovered in this way were 88 and 98 g. per 100 g. of coal and coke, respectively.

Esterification followed by distillation of the esters in a special molecular fractionating still resulted in the isolation of no crystalline material other than dimethyl oxalate. Separation of the acids on the basis of varying salt solubilities, followed by liberation of the free acids from the salt fractions, and esterification and fractionation of the esters, resulted in the isolation of small amounts, usually less than 2 g. per 100 g. of coal or coke, of various benzene carboxylic acids. The presence of a large fraction, approximately 50%, of esters which are not distillable, under conditions where it was shown that the esters of known carboxylic acids distil rapidly, has led to the conclusion that a significant part of the acids from this coal and coke are more complex than benzene carboxylic acids. The persistent yellow color of the acids and low volatility of the esters indicate that they may be condensed aromatic acids containing carbonyl oxygen. It is pointed out that the failure to recover hydrocarbons more complex than diphenyl, by decarboxylation, does not necessarily preclude the possibility of the presence of acids with condensed aromatic nuclei containing carbonyl oxygen, since drastic alkaline decomposition is known to split the nuclei of such aromatic acids.

PITTSBURGH, PENNA. RECEIVED NOVEMBER 27, 1936

[CONTRIBUTION NO. 173 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

The Mechanism of Vinyl Polymerizations[1]

BY PAUL J. FLORY

Nearly all compounds containing non-benzenoid carbon–carbon double bonds are capable of undergoing polymerization when subjected to suitable conditions. High molecular weight polymers may be formed from many such compounds, notable examples of which are styrene, vinyl acetate, acrylic acid and its esters, butadiene, and chloroprene. The closely similar characteristics of the conversion of monomer to polymer in these vinyl polymerizations has led to the conclusion that all of them proceed by essentially the same mechanism.

An abundance of evidence has been accumulated to show that typical vinyl polymerizations are chain reactions.[2,3] Except in the presence of certain polymerization catalysts, it may be assumed that the chain is propagated through the successive addition of monomer molecules to a free radical, *i. e.*

$$\text{---(CH}_2\text{—CHR)}_x\text{—CH}_2\text{—CHR—} \xrightarrow{+\ \text{CH}_2\text{=CHR}}$$

$$\text{---(CH}_2\text{—CHR)}_{x+1}\text{—CH}_2\text{—CHR—} \xrightarrow{+\ \text{CH}_2\text{=CHR}}$$

etc.[4,5]

In support of this free radical chain mechanism Taylor and Jones[6] have found that ethylene is polymerized by free radicals released in the thermal decomposition of metal alkyls, and Rice and Sickman[7] induced the polymerization of ethylene with methyl radicals from decomposing azomethane. The mechanisms of the equally important processes of chain initiation and termination have remained more obscure. From the limited experimental results available at the present time it is possible to draw certain general conclusions pertaining to the mechanisms of these processes, and upon the basis of these conclusions the theoretical treatment of the kinetics of vinyl polymerizations presented in the following pages has been developed.

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[1] The term "vinyl polymerizations" is used here to include not only polymerizations of derivatives of vinyl alcohol such as vinyl acetate or vinyl chloride, but all polymerizations involving olefinic double bonds and leading to products of high molecular weight.

[2] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, Oxford, 1935, p. 444.

[3] Chalmers, THIS JOURNAL, **56**, 912 (1934).

[4] Staudinger and Frost, *Ber.*, **68**, 2351 (1935).

[5] Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936).

[6] H. S. Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930).

[7] O. K. Rice and Sickman, *ibid.*, **57**, 1384 (1935).