is at a shorter wave length than that typical of the pure vinyl-conjugated ketone (*cf.* XVI, λ_{max} 269 mμ) and at a longer wave length than that of the nonvinyl conjugated ketones which absorb at 255 mμ. By using a standard method of two component analysis, with XIII and XVI as standards, it was calculated that the mixture consisted of 79% of vinyl ketone equivalent to XVII, and since one half of XXI is included in this figure, this agrees very well with the postulated composition of 60% of XVII and 40% of XXI.

The mixture could be stored in the cold without change for long periods of time, but when freed from inhibitor by thorough washing, it polymerized to a soft, rubbery material after 5 hours at room temperature. A sample was also polymerized as its potassium salt in water in the presence of potassium persulfate at 50°. After 19 hours the solution no longer decolorized bromine. λ_{max}^{MeOH} 258 mμ, ϵ 15,000.

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BOSTON, MASS.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORP.]

Catalytic Graphite Inclusion Compounds. I. Potassium Graphite as a Polymerization Catalyst

H. PODALL, W. E. FOSTER, AND A. P. GIRAITIS

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Potassium graphite, KC_8, has been found to catalyze the polymerization of ethylene at low pressure. The effects of various reaction conditions, including concentration of catalyst, catalyst support, and additives, were studied.

Alkali metals are known to catalyze the polymerization of ethylene.[1,2] However, high temperatures and pressures are generally required, and liquid rather than solid ethylene polymers are produced. While investigating the reactivity of various alkali metal compounds with olefins, it was surprisingly found that potassium graphite, KC_8, suspended in 2,4,4-trimethylpentane (isooctane) catalyzed the polymerization of ethylene at 200° and only 1000 p.s.i.g. pressure. The products were found to consist of C_8-C_{14} *trans*-monolefins and a small quantity of low molecular weight *solid* polyethylene. Infrared analysis of the polyethylene indicated it to be essentially linear. Consequently, it was of interest to explore the catalytic activity of potassium graphite and other graphite inclusion compounds in olefin polymerizations. This paper is concerned with results obtained with ethylene.

Reaction variable study. The polymerization of ethylene in isooctane or *n*-heptane by means of catalytic amounts of potassium graphite did not occur until a temperature of 180–200° was reached. Moreover, it appeared necessary to maintain this temperature for the reaction to continue. Use of long reaction times (five days) at lower temperatures, 120–150°, resulted in no significant polymerization.

In going from isooctane to *n*-heptane the yield and degree of polymerization showed a significant increase. Use of benzene, toluene, or isopropylbenzene as solvents resulted in alkylation of these substances. They therefore were not suitable as solvents for the polymerization reaction. The alkylation reactions will be discussed in a subsequent paper.

Upon increasing the concentration of suspended KC_8 catalyst, the yield of polymerized ethylene increased in both isooctane and *n*-heptane. However, upon going to a very concentrated slurry of catalyst, no significant polymerization occurred. It therefore appears that there must be present sufficient ethylene in solution so that the initiation and chain growth reactions can favorably compete with the termination reactions.

The greater effectiveness of the potassium graphite inclusion compound over other alkali metals as an ethylene polymerization catalyst could be due to the high surface area of the potassium in the inclusion compound. To test this idea, potassium was dispersed over potassium chloride in one experiment and over sodium monoxide in another experiment. Each of these systems was tested for catalytic activity with ethylene. As was expected, K/KCl also catalyzed the polymerization of ethylene. However, no solid polymer was produced, and the yield of polymerized ethylene was only about one-third that obtained with KC_8 under comparable conditions. The K/Na_2O showed no catalytic activity toward ethylene, in the absence or presence of isopropylbenzene.[3] A plausible explanation for this apparent discrepancy is that the potassium

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[1] H. W. Walker, *J. Phys. Chem.*, **31**, 961 (1927).

[2] K. Clusius and H. Mollet, *Helv. Chim. Acta*, **39**, 363 (1956).

[3] It is interesting to note that K/Na_2O very effectively metalates such alkylbenzenes as toluene and isopropylbenzene in the α-position [C. E. Claff and A. A. Morton, *J. Org. Chem.*, **20**, 440, 981 (1955)]. Consequently, it would appear that potassium isopropylbenzene is also a relatively ineffective ethylene polymerization catalyst.

atoms are sufficiently bonded to the oxygen of Na_2O so that they cannot interact with ethylene.[4]

Product distribution. The polymerization of ethylene by potassium graphite produces a mixture of products ranging from low boiling liquids to moderately high melting solids. The distillable liquids were found to consist primarily of C_8-C_{14} olefins, containing generally one double bond per molecule, as determined from their boiling points, refractive indices, and iodine numbers. Moreover, these olefins appeared generally to possess *trans* structures, according to their infrared spectra. The solid products were obtained partly from the residue of the distillation and partly from the graphite, by extraction of the latter with benzene or toluene, followed by precipitation with alcohol. The residue from the distillation was generally a brown tacky semisolid, whereas the solid obtained from the graphite resembled low pressure polyethylene according to its infrared spectrum and microscopic melting behavior (melting point approx. 120°.)

Attempts were made to increase the proportion of solid to liquid polymer by going to lower temperatures and longer reaction times, lower concentrations of suspended catalyst, and use of higher pressures. Only the second of these variables, *i.e.* lower catalyst concentration, gave any significant improvement. This apparent lack of dependence of product distribution upon the conditions used indicates that the distribution may depend upon impurities which short-stop the chain growth reaction. Alternately, the chain growth might be limited sterically if the chain growth, as well as initiation reaction, occurs within the framework of the inclusion compound.

The vent gas from the polymerization reaction was found to contain appreciable amounts of ethane, suggesting the presence of ethyl radicals or carbanions. In order to trap the alkyl carbanions, the reaction mixture of one experiment was carbonated with Dry Ice. A very small quantity of a brown solid, m.p. 160–167° dec., was isolated. Solubility and infrared spectral data indicated it to consist of a mixture of branched unsaturated carboxylic acids. The isolation of this material suggests the formation of alkylpotassium compounds during the course of the polymerization reaction. This is further indicated by the fact that the potassium graphite is partially consumed during the reaction, as evidenced by the decreased reactivity of the reaction mixture towards water at the end of the reaction; quenching with water gives less hydrogen than expected if the KC_8 behaved as a true catalyst, and gives mainly liquid or solid hydrocarbons. The latter probably arise from long chain alkylpotassium compounds.

Effect of additives. Polymerization was speculated to occur through carbanion intermediates. It was felt that the low yield of polymer might be due to the inability of potassium graphite to produce free alkylcarbanions readily under the conditions used. Some attempts were therefore made to modify the potassium graphite system, by adding various substances which would lead to reactive alkylcarbanions.

It was found that ethylpotassium prepared *in situ* from diethylzinc and excess potassium graphite polymerized ethylene under relatively mild conditions to give a mixture of liquid and some solid polyethylene.[5] Alternately, diethylzinc and potassium triethylzinc, prepared *in situ* from *excess diethylzinc* and potassium graphite, were each ineffective for polymerizing ethylene under the same conditions. These results suggest that it is necessary for the ethylcarbanions to be relatively free, or unbonded, in order for polymerization to occur readily. This consideration may apply to interpreting the function of titanium salts with triethylaluminum in the Ziegler process for polyethylene. The titanium salts could react with triethylaluminum, forming weak ethyl to titanium bonds which readily dissociate to form ethylcarbanions. Allyl chloride, isopropylbenzene, and titanium tetrachloride[6] were tested as additives without success.

Typical results obtained in this study are shown in Table I.

EXPERIMENTAL

Preparation of potassium graphite, KC_8. A 3-neck 300-ml. round-bottom flask was equipped with a stainless steel scraper stirrer (air driven), metal thermometer, and a port with a side arm for the introduction of potassium and a continuous stream of nitrogen, respectively. The apparatus was then flamed dry under a stream of nitrogen. Dixons Microfyne graphite, 25 g. (2.08 g.-atom) was then added to the flask and the system again flamed dry under nitrogen. Potassium (C.P. reagent), 10.1 g. (0.26 g.-atom), cut into small pieces under Bayol-D and rinsed with *n*-pentane, was then added to the well stirred graphite at 275 ± 20° over a period of 40 min. The reaction is exothermic, and the potassium is therefore added at a slow enough rate to insure complete reaction before addition of more potassium. The product, KC_8, is a fine bronze-colored powder which sparks in contact with air and can be handled safely in an atmosphere of dry oxygen-free nitrogen, or possibly argon. The preparation and properties of potassium graphite have been

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[4] An alternate explanation is that potassium reduces sodium monoxide to sodium under the conditions used, and that the latter is ineffective for polymerizing ethylene.

[5] Comparable data for the polymerization of ethylene in the presence of pure ethylpotassium could not be found.

[6] It has been pointed out by one of the referees that the failure of the KC_8-$TiCl_4$ system to catalyze the polymerization of ethylene is surprising in view of the reported catalytic action of the isoamylsodium-$TiCl_4$ system on the polymerization of ethylene. [C. D. Nenitzescu, C. Huch, and A. Huch, *Angew. Chem.*, **68**, 438 (1956)]. Our experiment on the KC_8-$TiCl_4$ system was conducted using approximately 1.6 g.-atom. of potassium/mole $TiCl_4$. Consequently, it is possible that all of the KC_8 was consumed upon contact with $TiCl_4$, leaving none available for the formation of the postulated ethylpotassium intermediate.

TABLE I

POLYMERIZATION OF ETHYLENE BY POTASSIUM GRAPHITE (KC_8)

					Products, G./G. K		
Catalyst, G., KC_8	Solvent, Ml.	Temp., °C.	Time, Hr.	Pressure,[a] (P.S.I.G.)	Liquid polymer	Solid polymer residue[b]	Extractable solid polymer[c]
36.0	300 isooctane[d]	200	6	1000	1.1	—	0.18
12.0	100 isooctane	200	22	1000	3.5	0.8	.14
1.2	100 isooctane	200	4	1000	—	No reaction	—
15.0[e]	100 isooctane	200	20	1000	1.6	0.6	None
6.0	100 *n*-heptane	200	21	1000	6.9	1.3	<0.3
8.0[f]	20 *n*-heptane	200	24	900	—	No reaction	—
3.0	7 *n*-heptane	200	42	1000	—	No reaction	—
6.8+ 2 ml $ZnEt_2$	10 *n*-heptane	200	50	1000	7.5	3.1	0.25
3.4+ 4 ml $ZnEt_2$	20 *n*-heptane	200	7.5	1000	—	No reaction	—
4 ml $ZnEt_2$	20 *n*-heptane	200	7.5	1000	—	No reaction	—

[a] Maximum pressure during run. [b] Residue from distillation of liquid polymer. [c] Solid extracted from graphite. [d] "Isooctane" or 2,2,4-trimethylpentane. [e] Grams of K/KCl from 4 g. K dispersed over 20 g. KCl. [f] Grams of K/Na_2O from 5 g. K dispersed over 40 g. Na_2O.

TABLE II

RECTIFICATION DATA FOR A TYPICAL RUN[a]

Fraction	B.P.,[b] °C.	Wt., G.	n_D^{25c}	Composition[d]	Double Bonds[e] per Molecule	Probable Identity
1	80	121.5	—	Benzene	—	Benzene
2	80–99	11.6	—	—	—	—
3	99–120	0.80	1.4376	Benzene + α-olefin	—	—
4	120–154	.79	1.4111	α-olefin + *trans*	—	—
5	154–155	.71	1.4208	α-olefin + *trans*	0.9	Octenes
6	155–169	.45	1.4235	α-olefin + *trans*	—	—
7	169–193	.50	1.4255	*Trans* olefin	1.2	Decenes
8	193–206	.72	1.4298	*Trans* olefin	—	—
9	206–235	.58	1.4350	*Trans* olefin	1.1	Dodecenes
10	235–300	.92	1.4462	*Trans* olefin	—	—
11	>300	.31	1.4623	*Trans* olefin	1.4	Tetradecenes
Residue	>300	1.3	—	—	—	—

[a] From second run shown in Table I. [b] Corrected to 760 mm. by vapor pressure nomograph. [c] Corrected to 25°C. [d] Major structural components as indicated from infrared spectra. [e] Calculated from iodine number assuming product is olefin shown in column 7.

previously described by Fredenhagen, Herold, and others.[7]

Preparation of potassium on potassium chloride. Potassium chloride, (C.P.) was dried at 110° for 3 hr. and then ball milled to fine powder. The same apparatus as described above was here used for dispersing potassium on potassium chloride. Four grams of potassium were added piecewise to 20 g. of KCl at 120–150° over a period of 1 hr., with vigorous stirring. After 3 g. of potassium had been added, the solid product became chunky and difficult to agitate. The product was a gray chunky solid. It is recommended for future purposes that 7 to 8 parts of KCl be used per part of dispersed potassium.

Preparation of potassium on sodium oxide. Sodium oxide, Na_2O, was predried at 200°. Five grams of potassium was then added piecewise, as in the above procedures, to 40 g. of sodium oxide at 200–250° over a period of 1.5 hr. with vigorous stirring. The product was a brown powdery solid.

All of the above materials were stored and handled in a dry box using dry oxygen-free nitrogen.

Use of modified KC_8 catalysts. The general procedure was to add first the desired quantity of solvent to the autoclave bomb, followed by addition of a predetermined quantity of potassium graphite, and then by the additive. The operation was, of course, carried out in the dry box.

Polymerization procedure. A 100-ml. or 250-ml. Magne-Dash autoclave was disassembled, rinsed with acetone or another appropriate solvent, and dried under an atmosphere of dry nitrogen before each run. The body of the autoclave was then charged with the desired quantity of solvent and catalyst and stoppered in the dry box with a rubber stopper. The body was then fixed to the autoclave head in an atmosphere of nitrogen. The autoclave was then purged three times with 200 p.s.i.g. C.P. ethylene (Matheson) and then pressurized to 400–500 p.s.i.g. Heating was then begun until the pressure rise began to slacken, or until 300° (maximum temperatures used), and the body then maintained at this temperature. The temperature was measured by means of iron-constantan thermocouples hooked to a Leeds-Northrup portable potentiometer and was controlled manually by means of a Variac. The pressure was measured with a Bour-

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(7) K. Fredenhagen and G. Cadenbach, *Z. anorg. u. allgem. chem.*, **158**, 249 (1926). A. Schleede and M. Wellmann, *Z. physik. Chem.*, **B18**, 1 (1932); A. Herold, *Compt. rend.* 232, 838–9 (1951); A. Herold, *Bull. soc. chim. France*, 999–1012 (1955).

don gauge. The system was periodically repressurized to 800–1000 p.s.i.g. when the pressure would drop below 400–500 p.s.i.g. When no further pressure drop occurred the system was cooled to room temperature by means of an air jet, and a sample of vent gas was generally taken for mass spectral analysis. The mixture was then quenched with alcohol or water and then filtered to remove solid material. The graphite filter cake was then washed or Soxhlet-extracted with benzene or other aromatic hydrocarbons. The organic layer was dried over Drierite and then fractionally distilled through a 3-ft. concentric tube column, or "drowned-out" by the addition of some 2B-ethyl alcohol. The fractional distillation was carried out at atmospheric pressure until decomposition was evident, and then continued under reduced pressure to avoid excessive decomposition. Refractive indices of the various fractions and their infrared spectra were then obtained. In certain cases iodine numbers were also obtained. The rectification data of a typical run is shown in Table II.

Typical example. Six grams of KC_8 and 100 ml. of heptane (Phillips, 99 mole %, dried over CaH_2) were charged into a 250-ml. Magne-Dash bomb. The bomb was secured to the autoclave head and the system purged with ethylene. The bomb was then charged with 500 p.s.i.g. ethylene at 20° and then heated. At about 190° and 900 p.s.i.g., a slightly exthermic reaction set in with a gradual uptake of ethylene. The system was maintained at 200° for 21 hr. with periodic repressurizing with ethylene to maintain an ethylene pressure of 500 p.s.i.g. or greater. The system was then cooled to room temperature, quenched with 50 ml. water, and filtered. The heptane layer was dried over Drierite and then rectified. Twelve grams of distillate (b.p. 115–280°, corr. to 760 mm.) in excess of the heptane fraction was obtained (or 6.9 g. per g. potassium). The distillate consisted of a complex mixture of mainly C_8 to C_{14} monolefins, probably *trans* isomers (as determined by the boiling points, refractive indices, infrared spectra, and iodine numbers of the various fractions). The residue of the distillation, a dark brown tar, (b.p. >280°/760 mm.) amounted to 2.3 g. (or 1.3 g. per g. potassium). The graphite filter cake was then extracted with 100 ml. of *m*-xylene for 6 hr. by means of a Soxhlet extractor. The extract was then evaporated to dryness yielding about 0.5 g. of waxy solid (or 0.3 g./g. potassium). Infrared spectra of this solid indicated it to be low molecular weight linear polyethylene.

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BATON ROUGE, LA.