Interaction between Acrylonitrile and Amorphous Carbons.

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Degassed sugar-chars and certain carbonized coals have been found to cause slight polymerisation of acrylonitrile at 60°. Carbon " activated " by being heated in moist air does not initiate polymerisation in the dark, and inhibits photopolymerisation unless traces of oxygen are present, whereupon a photosensitive material is formed, and extensive polymerisation occurs. These results are related to the paramagnetic resonance absorption of the carbons.

CERTAIN forms of amorphous carbon and coal are paramagnetic (Bennet and Ingram, *Phil. Mag.*, 1954, **45**, 545; Ingram and Tapley, *ibid.*, p. 1221; Ingram, Tapley, Jackson, Bond, and Murnaghan, *Nature*, 1954, **174**, 797; Garten and Weiss, *Austral. J. Chem.*, 1955, **8**, 68). It is well known that free radicals are paramagnetic, and that sufficiently reactive radicals, formed in the presence of certain vinyl monomers, will initiate polymerisation. The object of this work was to discover whether carbon surfaces initiate polymerisation and, if so, under what conditions.

Few studies of catalysis of polymerisation of vinyl compounds by solids have been reported. Paravano (*J. Amer. Chem. Soc.*, 1950, **72**, 3856, 5546) found that some surfaces, including carbon, while not themselves capable of initiating polymerisation, can indirectly catalyse the polymerisation of aqueous methyl methacrylate when certain reactions are proceeding on the surface. Unfortunately the nature of the carbon used in these experiments was not stated. He postulated that polymerisation was initiated by active radical intermediates which occasionally escaped from the surface. Markham and Laidler (*J. Phys. Chem.*, 1953, **57**, 363) found that aqueous suspensions of zinc oxide irradiated with ultraviolet light (largely 3650 Å) could initiate the polymerisation of methyl methacrylate and acrylonitrile. No polymerisation occurred in the absence of zinc oxide. However, a short induction period was observed, and these authors suggest that, despite careful precautions, some oxygen may have been present. They postulate that, as a consequence of light absorption, an electron is transferred from the catalyst to a water molecule, with consequent formation of a hydrogen atom. It seems, however, that the significance of these results is limited since, if oxygen was present, some hydrogen peroxide would have been formed and its photolysis could have initiated the polymerisation.

One instance when radicals present in the solid phase initiate polymerisation is described by Bamford and Jenkins (*Proc. Roy. Soc.*, 1953, *A*, **216**, 515; 1955, *A*, **228**, 220), who found that coagulated solid polymer formed during the photo-polymerisation of pure acrylonitrile at room temperature could initiate further polymerisation, in the dark, on being warmed to 60°. These, and other results (Bamford and Barb, *Discuss. Faraday Soc.*, 1953, **14**, 208), led them to postulate that growing polymer radicals had become trapped in the coagulated polymer in such a way that monomer could only diffuse to the radicals at an elevated temperature. This catalysis was suppressed when oxygen was admitted to the system. In agreement with this theory, a small but definite paramagnetic resonance absorption has been observed in a specimen of polyacrylonitrile formed in this manner (Bamford, Jenkins, Ingram, and Symons, *Nature*, 1955, **175**, 894).

EXPERIMENTAL

Materials.—Sugar char, designated " C_s," was prepared by carefully heating " AnalaR " sucrose in an all-glass system *in vacuo* to 400° until a pressure of 10^{-4} mm. could be maintained. In some experiments the resulting char was cooled and ground to a fine powder before use, in others the specimen was used directly without exposure to oxygen. The results were qualitatively the same with either procedure. Two samples of sugar char, both referred to as C_a, were activated at 400° and 550° respectively in a stream of moist air for 13 hr. (Garten and Weiss, *loc. cit.*). Two coal specimens, C_c, were carbonized at 510° and 520° respectively in nitrogen for 45 min. Acrylonitrile was purified by being shaken with dilute sulphuric acid, dilute sodium hydroxide, and purified water, dried ($CaCl_2$), and de-aerated by repeated distillation *in vacuo* into tubes cooled in liquid oxygen. Water was distilled from, and glass-ware was cleaned with, alkaline permanganate. *In vacuo* refers to a pressure between 10^{-4} and 10^{-5} mm.

Procedure.—The carbon (*ca.* 0·1 g.) in a Pyrex tube (¼ in. diameter) was gradually heated to 400° *in vacuo* until evolution of gas ceased. After immersion of the tube in liquid oxygen, pure de-aerated acrylonitrile was allowed to pass into it so that, on melting, there was a ½ in. layer of momomer above the carbon. The mixtures were shaded from direct sunlight, since, under certain conditions, ultraviolet light was found to catalyse the initiation of polymerisation. There was no apparent change after 24 hr. at room temperature, but with C_s and C_c, on warming to 60°, a cloudy suspension of polymer grew from the surface of the carbon, and within a few minutes had spread vertically through the monomer. Sometimes a small flocculent precipitate settled on the carbon surface before polymerisation ceased. A rough estimate based on the turbidity gives the overall conversion into polymer as 0·1%. The whole of the reaction tube, including the upper part filled with vapour, was warmed to 60° : if only the liquid was warmed some boiling occurred with agitation of the liquid. Under these conditions no polymer was seen, probably because it adhered to the rapidly moving carbon particles. Paravano (*loc. cit.*) also found that the liquid must be stationary for polymerisation to be observed. In the dark, a trace of oxygen prevented polymerisation.

In other experiments the acrylonitrile–carbon mixtures were irradiated at room temperature with ultraviolet light filtered through Pyrex glass from a medium-pressure 250-w mercury arc 9 in. from the specimen. Under these conditions pure acrylonitrile, in the absence of carbon, polymerised very slowly, and was used as a control. This natural rate of polymerisation was not altered by C_s or C_c, but the " activated " steam-treated carbons acted as inhibitors and no turbidity could be seen after 12 hr. However, a slight yellow colour was then apparent, and filtration and vacuum-distillation yielded a trace of high-boiling oil which was probably a polymer of low molecular weight, soluble in the monomer.

When irradiated mixtures were freely and continuously exposed to air, no polymerisation occurred. If, after exposure to air, and before irradiation, the mixtures were throughly degassed by repeated freezing *in vacuo*, irradiation produced rapid and extensive polymerisation, which was shown to be due to a soluble, photosensitive substance, since rapid polymerisation occurred in the liquid after decantation from the carbon. For results see Table.

Polymerisation of acrylonitrile in presence of carbons.

	Oxygen-free * in dark, 60°		Irradiated, 20° Time to first turbidity and subsequent rate	
Carbon	Time to first turbidity	Approx. % polymer at completion	Oxygen-free	In presence of trace * of oxygen
C_s	Immediate	0·1%	5 min., slow	1 min., rapid
C_c	Immediate	0·1%	5 min., slow	1 min., rapid
C_a	No polymerisation		No polymerisation	2 min., rapid
Nil	No polymerisation		5 min., slow	5 min., slow

* With *free* exposure to air no polymerisation occurred on any of the carbons.

In an attempt to discover what soluble, photosensitive material can be liberated from oxygenated carbon, the ultraviolet absorption spectra of aqueous extracts from various carbons were examined with a Unicam SP 500 quartz spectrophotometer. The water was de-aerated by repeated partial freezing and distillation *in vacuo*, and distilled on to the de-aerated carbon prepared as above. The extract from carbons which had never been exposed to oxygen had an absorption spectrum identical with that of water. When oxygen had been admitted before filtering off the carbon the absorption was generally similar to that of a dilute solution of hydrogen peroxide, except that absorption was rather stronger from 200 to 220 mμ. Since it was thought likely that traces of oxalic acid were present (King, *J.*, 1933, 842; 1934, 22) attempts were made to reproduce the curve obtained from the extract by mixing hydrogen peroxide with oxalic acid. It was ultimately found that a solution 10^{-4}M in hydrogen peroxide and $1\cdot2 \times 10^{-3}$M in oxalic acid gave a curve almost identical with that obtained from the carbon extract in the 200—300 mμ region. The extracts from different forms of carbon had substantially the same ultraviolet absorption. The inference that hydrogen peroxide and oxalic acid were present was supported by the following tests made on the aqueous extracts: Cold acidified potassium permanganate solution was immediately decolorised, a blue colour at once appeared in a starch–iodide solution, and a faint but definite precipitate was obtained from a calcium chloride solution. Various spot-tests for formic acid were inconclusive.

For measurement of paramagnetic resonance absorption the monomer was removed by distillation *in vacuo*, and the tube with the carbon placed in an H_{012} 3 cm.-wavelength rectangular resonant cavity at room temperature. All the carbons retained a strong absorption, showing that only a small percentage of the radical centres had beeen involved in the polymerisation. The intensity of the signal was always less than that of the original carbons, but quantitative interpretation of the measurements is not practicable since the strength of the signal depends on the concentration of the carbon, which had been altered through aggregation of the particles, and may also be affected by acrylonitrile polymer adhering to the carbon.

The effect of admitting air to the carbon, before and after treatment with acrylonitrile, was also observed. On admission of air to a carbon not previously in contact with acrylonitrile the strength of the signal decreased suddenly (Ingram and Tapley, *Chem. and Ind.*, 1955, 568). The percentage decrease varied with the nature of the carbon and its previous treatment but was always more than 50%. When air was admitted to a carbon previously treated with acrylonitrile, the signal very slowly decreased by not more than 5%. The inference is that the pores of the carbon are clogged with acrylonitrile, preventing the adsorption of oxygen.

DISCUSSION

The fact that oxygen-free carbons initiate polymerisation in the dark shows that active free radicals must be present in the carbon. This polymerisation does not extend visibly into the liquid below about 60°; at room temperature no more than a slightly increased tendency of the carbon particles to adhere is observed. Probably polymerisation proceeds in the pores of the carbon at room temperature but cannot easily continue out into the liquid until the temperature is high enough for molecules of monomer to penetrate the polymer and reach the free radicals in the pores.

All the chars consist of multinuclear aromatic ring systems (Riley, *Quart. Rev.*, 1947, **1**, 59). The radicals probably present may be divided into two classes: first, stable, benzyl-type radicals in which the orbital of the single electron can overlap efficiently with the π-orbitals of the ring system to which the carbon carrying the single electron is attached; such radicals would probably be ineffective as initiators of polymerisation and might well act as inhibitors (Burnett, "Mechanism of Polymer Reactions," Interscience Publishers Ltd., 1954, p. 84). Secondly, reactive phenyl-type radicals in which the unpaired electron is localised on one carbon atom might well remain in the rigid network if pyrolysis proceeds by homolysis of bonds. Ingram *et al.* (*locc. cit.*) estimate that the ratio of carbon atoms to unpaired electrons in coals and carbons similar to those used here is about 1600, but it is probable that many active centres are in positions inaccessible to the monomer or other adsorbates.

Garten and Weiss (*loc. cit.*) suggest that the paramagnetism of amorphous carbons arises because some of the multinuclear ring systems have a slightly semiquinone character. The presence of oxygen is however not necessary for paramagnetic resonance, since Bennett, Ingram, and Tapley (*J. Chem. Phys.*, 1955, **23**, 215) found that chars obtained *in vacuo* from hydrocarbons have the same distinctive paramagnetic properties. They have also stressed that the small paramagnetic resonance found in graphite (Castle, *Phys. Rev.*, 1953, **92**, 1063; 1954, **94**, 1410) has quite different characteristics from that of amorphous carbons. It therefore seems likely that slight unparing of the π-electrons in large multinuclear structures makes little contribution to the paramagnetism observed in amorphous carbons.

The fact that " activation " by treatment with moist air destroys the power of initiating polymerisation in the dark, and also prevents photopolymerisation, may be due to the presence of phenolic groups on the carbon. Garten and Weiss (*loc. cit.*) give evidence that such " activated " carbons contain a number of phenolic hydroxyl and quinone groups.

The formation of oxalic acid when carbon is treated with water and oxygen was previously observed by King (*J.*, 1933, 842; 1934, 22). Among others, Garten and Weiss (*loc. cit.*) have postulated the formation of hydrogen peroxide, for which evidence is given here, but the mechanism of its formation is still obscure. It might possibly arise from reaction of molecular oxygen with hydrogen attached to the carbon. An alternative possibility is the reversible formation of the radical $\vdots C{\cdot}O{\cdot}O{\cdot}$, as postulated by Bamford, Jenkins, Ingram, and Symons (*Nature*, 1955, **175**, 894) for the first stage of the interaction between oxygen and acrylonitrile radicals. This could subsequently react with water or mobile organic molecules to give a peroxide. Possibly the quenching effect of oxygen on the paramagnetic signal is due to the formation of this or a similar radical on the carbon surface. The superoxide radical ion O_2^- has a very broad paramagnetic absorption band (Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443): if the $\vdots C{\cdot}O{\cdot}O{\cdot}$ radical has a similar broad absorption band this would account for the quenching of the narrow band found with oxygen-free carbon.

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