The mechanism of the thermal resinification of pure furfural

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ABSTRACT. Samples of pure furfural were heated *in vacuo* at 100-250°. The reactions leading to colour and resin formation were studied by isolating and characterizing the intermediate products; the rate determining step of the process seems to be a surface-catalyzed condensation reaction. The resins obtained owe their very dark colour to the presence of unpaired electrons delocalized over various structures which include furan and dihydrofuran rings and carbonyl groups. The insoluble, black resin which constitutes the final product is formed through a steady-state, complex mechanism.

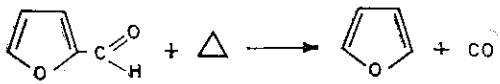
RESUMEN. Se sometieron muestras de furfural puro a calentamiento bajo vacío a 100-250°. Las reacciones responsables de la formación de color y de resina fueron estudiadas mediante el aislamiento y la caracterización de los productos intermediarios; el paso lento del proceso parece ser una reacción de condensación catalizada por la superficie del reactor. El color muy oscuro de las resinas obtenidas se debe a la presencia de electrones no pareados, deslocalizados sobre múltiples estructuras, tales como anillos furánicos y dihidrofuránicos y grupos carbonilos. La resina negra e insoluble que constituye el producto final se forma a través de un mecanismo complejo que involucra el establecimiento de un estado estacionario.

INTRODUCTION

Usually organic compounds undergo pyrolysis into smaller fragments through molecular or radical chain-reactions at temperatures above 250°, while at lower temperatures they can suffer molecular rearrangements or condensations to produce isomers, polymers and resins.

It is common to find in these reactions that the nature of the vessel's inner surface plays an important catalytic role in determining the kinetics of the products' formation and this has been a traditional source of irreproducibility of the results, since it is difficult to guarantee identical surfaces from one experiment to the next or from one study to another.

The present paper deals with the thermal resinification of liquid furfural at relatively low temperatures. The gas-phase pyrolysis of this compound (in the presence or absence of catalyst) is well known and has been used to produce furan on a commercial scale[1]:



Several occasional mentions to the thermal resinification of furfural appear in the literature, but in fact only one study has been published where the experiments were carried out in an inert atmosphere, thus avoiding oxidation, which is a much more serious source of resinification. In that study[2], furfural was heated at 140-230° and the percentage of resinification, together with the increase in acidic products, were determined as a function of the reaction time and temperature. From the results obtained, the authors concluded that furfural is reasonably stable from the point of view of its use in industrial processes involving exposures at high temperatures for fairly short times, since the calculated losses due to resinification were very small. No mention was made of the possible mechanism leading to the formation of the black, insoluble resins nor to their structure.

In this work we present evidence which gives some insight into the nature of the reactions involved in these thermal processes.

EXPERIMENTAL

All experiments were carried ou *in vacuo*, taking particular care to remove oxigen, water, acids and other contaminating substances from the reaction medium. The vacuum system used was a standard one (10^{-5} — 10^{-6} torr); which made it possible to carry out all manipulations preceeding and following the actual reactions without the interference of oxidations products.

Furfural. Commercial samples (B.D.H. or Reachin) of about 500 ml. were shaken with activated charcoal to remove part of the coloured resins and then with sodium carbonate to neutralize any acidic impurity. They were then twice distilled at reduced pressure (ca. 0.2 torr) in a stream of dry nitrogen (generous heads and tails being discarded in each distillation); the first central portion was collected over calcium chloride

and the second over calcium hydride. The latter was transferred to the vacuum line, throughly degassed and dried and finally vacuum distilled to a reservoir provided with a Hoke metal-valve. Samples for all the experiments to be described were withdrawn from that reservoir and vacuum distilled into the reaction vessel. If properly protected from the light, the furfural thus obtained remains colourless and does not suffer any change in purity; in fact g.l.c. analysis consistently gave a single peak, no residual acidity was detected upon titration and the refractive index at 20° gave a reproducible value of 1.5260.

Other authors [3] have reported purification procedures for this compound, but we feel that high-vacuum handling and storage are essential to guarantee the preservation of this purity for longer than a few days.

All other reagents used were best-grade commercial products.

Working Procedures. Typically, about 2 ml, of pure furfural were vacuum distilled into a pyrex tube provided with a break-seal; after sealing off, the tube was placed in an oven which was kept at the desired temperature (± 1°) and left for a period of time which varied from several hours to months, depending upon the reaction temperature. At the end of this thermal treatment, the products were separated according to the procedure shown in (Table I). In order to accumulate larger amounts of some intermediate products, we also carried out some reactions with much larger quantities of furfural (100 — 250ml), keeping however the same conditions as described above.

TABLE I

Separating procedure

Reacted Mixture:	Gaseous products. They are identified by mass spectrometry and analysed by G.L.C.
	Liquid products. They are separated by difference in volatility identified by spectroscopic and chemical characterization and analysed by G.L.C.
	Solid products. They are separated by sublimation and by difference in solubility. They are characterized by spectroscopy and physical properties and analysed by weighing.

The changes in colour and in electrical conductivity were followed in the device shown in (Fig. 1). The spectrum and the resistance were measured periodically at room temperature by tipping some of the liquid through the sintered-glass filter into the cell. The liquid was then tipped back into the reaction tube and the device placed back into the oven. Only visible spectra were recorded (at first with the 10mm cell, then as the colour deepened, with the 1mm one), since liquid furfural cuts off at about 390 nm. The experiment with gaseous furfural was conducted in a 2 liter flask provided with a small tube for condensation (about 5 ml. of liquid) and with a break-seal.

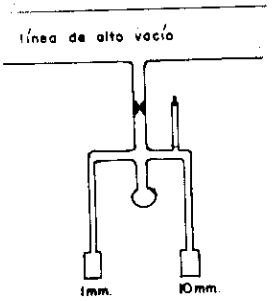


Fig. 1. Device used in the spectroscopy-conductivity experiment.

All experiments with surfaces other than pyrex were carried out together with a control experiment in pyrex, to make comparisons more direct and meaningful.

Instruments. Following is a list of commercial instruments used in this work: UNICAN SP 200 for infrared spectra; UNICAM SP 700 and SP 800 for ultraviolet and visible spectra; HITACHI F-60 for proton magnetic resonance spectra; HITACHI RMV-60 for mass spectra; HITACHI F-6 for gas-liquid chromatograms; KNAUER vapour pressure osmometer for number-average molecular weights and a model-27 conductimeter from the People's Republic of China for resistance measurements. The electron paramagnetic resonance spectra were taken at the Physics Dept., university of Essex, U.K.

RESULTS AND DISCUSSION

General Phenomenology. No apreciable changes were detected in the physical properties of furfural heated at 65° for several weeks. At 100°,

furfural goes through a sequence of colour changes (involving extremely small conversions) before the first traces of black, insoluble resin begin to appear on the walls of the reaction vessel. After about one week's treatment, it begins to turn yellow then it becomes pink, mauve and finally dark brown, at this point the process has concluded its first phase and from then on no further changes in colour are noticed, but the insoluble resin begins to accumulate. At higher temperatures (130 — 250°), one notices the same phenomena, but they become less well-defined because of the higher rates involved. Thus, at 200° the yellow colour appears within hours and it soon becomes difficult to apreciate any further change in shade because the insoluble resin precipitates not only on the walls but also as a fine powder within the reacting liquid.

The overall activation energy for the process appears to be high, judging from the marked increase in the rate of colour formation with the reaction temperature. It was imposible however to obtain any acceptable valve for this parameter because although the qualitative features of these reactions were reproducible, the time intervals for the various changes varied considerably among apparently identical experiments.

No increase in the viscosity of the reacting furfural was ever observed, even in reactions which were allowed to reach an advanced stage of resinification.

The acidity did not increase during the course of these thermal treatments.

The analysis of the products always gave very small amounts of carbon monoxide and furan in equimolar quantities; these compounds originated from the molecular decomposition shown in reaction I. The other products detected in all experiments were: water (appearing as an upper layer in the reactions at high temperatures and with longer times), a white sublimate which reached the upper walls of the vessel once all the volatile materials had been distilled off, an oily liquid with very low vapour-pressure, and a mixture of resins.

Some typical results are reported in (Table II and III). These data have been chosen at random from those of some 25 experiments carried out at different temperatures, with various reaction times and different initial quantities of furfural. The overall conversions were always low, i.e. furfural is resistant to changes under the working conditions chosen here; this confirms the observations of Dunlop and Peters.[1,2]

TABLE II

Some typical results

Temperature (°C)	100	150	200
Initial furfural (g)	1.0	1.6	35
Reaction time (hours)	1200	430	170
Furan/Furfural (molar ratio)	10^{-4}	10^{-3}	—
CO/Furan (molar ratio)	1.0	1.0	—
Total resin (% conversion)	0.1	0.1	2.0

TABLE III

Results of a typical reaction with a large quantity of furfural

	Gaseous product:	
		CO.
	Liquid products:	
Furfural (200 g) 170°, 500 hours		Furan, water (0.02 moles) and oily liquid (0.1 g).
	Solid products:	
		White sublimate (0.05 g), methanol-soluble resin (0.15 g), dichloromethane-soluble resin (0.15 g), and insoluble resin (4.23 g).

It was noticed that only the yields of water and of insoluble resin depended markedly on the reaction time; the amounts of sublimate, oily liquid and soluble resins, after an initial build-up, did not increase appreciably

with time. This is typical of a system involving stationary conditions and a confirmation of this phenomenon is shown in (Fig. 2) where the progress of a reaction at 100° is given in terms of optical densities at various wavelengths *vs* time. The levelling-off point corresponds to the attainment of the dark-brown colour and to the first appearence of insoluble resin; from then on the colour did not undergo any further change and the precipitate accumulated on the walls. During this run the electrical conductivity was also monitored and it was found that it remained practically constant, fluctuating around a value of 5×10^{-6} Mho/cm.

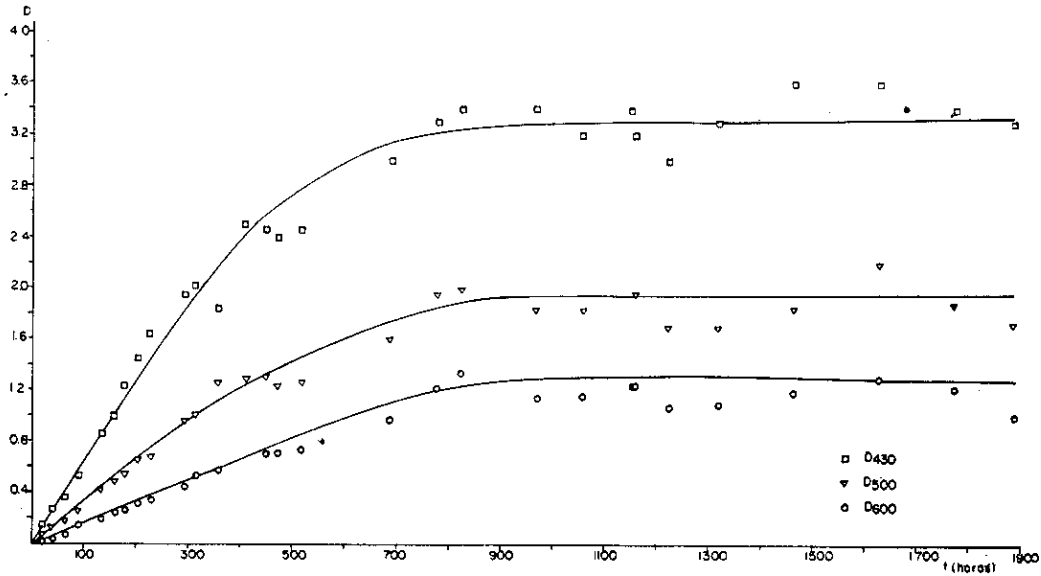
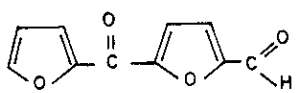


Fig. 2. Kinetics of colour development at different wavelengths for a reaction at 100°.

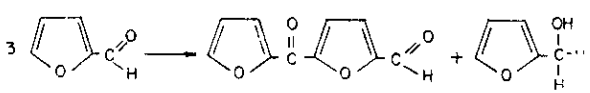
It was noticed that the insoluble resin often begun to appear at specific sites on the vessel's surface such as the sealed-off tip of the tube or the graded seals used in the device shown in (Fig. 1).

Products Characterization. The quantitative determination of water was carried out by vacuum-distilling the volatile products on to calcium hydride in a system of known volume connected to a mercury manometer. After all the water had reacted, a steady pressure of hydrogen was obtained and measured. Calculations showed that on the average one mole of water had been formed for every two to three moles of furfural consumed in the overall process, depending upon the conversion attained.

The white, cristalline sublimate was a stable compound melting at 125°. Its spectra gave the following features: i.r. (KBr),two carbonyl bands (1 680 and 1 640 cm^{-1}), the typical bands of the furan ring and of the aldehidic C-H, and a band at 970 cm^{-1} characteristic of 2,5-disubstituted furans; u.v. (ethanol), a shoulder at 285 mm and a maximum at 318 mm; p.m.r. ($CDCl_3$), six protons, one at τ 0.1 (adehyde), an AB system at τ 2.35 — 2.65 (olefinic or furanic), two in the range τ 2.2 — 2.3 (typical of protons 3 and 5 of the furan ring) and one at τ 3.3 quadruplet, (proton 4 of the furan ring), all with respect to TMS; mass, parent peak at m/e = 190, a strong fragment at m/e = 95 and the classical fragmentation pattern of furan derivatives and of furfural. The osmometric molecular weight gave 195 ± 10. From the above evidence we propose the following structure.



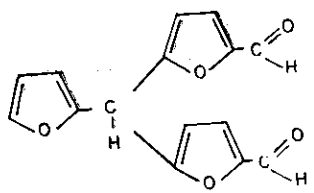
This compound, 5-furoylfurfural, has not been reported previously, but its isomer, 3-furoylfurfural, was recently synthesized and characterized by Zaluski et al.,[4] who only give the i.r. bands at 1 670 and 1 630 cm^{-1} for the two carbonyl groups. The origin of this product in the present reaction could be an oxidation — reduction of the type:



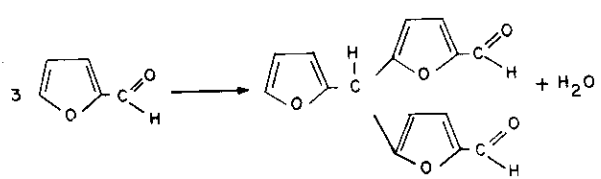
(II)

The absence of furfuryl alcohol among the products is not surprising considering that a) we might have missed it due to its vapour pressure which is similar to that of furfural itself (note the small yields in sublimate and therefore in furfuryl alcohol) or b) it could have participated in the resinification reactions (its reactivity in this sense is well known).

The oily liquid, always obtained in very small yields was unstable in the pure state, even when kept under vacuum; it turned dark brown within hours and resinified completely within a day at room temperature. Its i.r. spectrum (liquid) gave a single carbonyl band at 1 680 cm^{-1}, the typical bands of the furan ring, including a strong one at 970 cm^{-1} (2,5-disubstituted rings); also, a band at 2 850 cm^{-1} (aldehidic C-H) and a weak one around 2 930 cm^{-1} (aliphatic C-H). The u.v. spectrum gave a maximum at 285 mm (ethanol), similar to that of 5-methylfurfural. From this scarce evidence we tentatively propose the structure:



considering that it would agree with the spectroscopic findings and moreover that it would account for the condensation which takes place in the process. This compound in fact, could arise from the condensation of three molecules of furfural according to the following reaction:



(III)

This reaction has been discussed in the past within the context of the resinification of furfural by acids[5,6] but no attempt had ever been made to isolate its product. The inherent instability of 5,5'-diformyltris (2-furyl) methane is probably due to the lability of the tertiary hydrogen atom; it is known that di-and trifuryl carbinols are unstable and prone to rapid, spontaneous resinification.[7,8,9]

As shown in (Table III)), the resinous products of these thermal reactions can be separated into three fractions, namely:

1. a viscous orange-brown resin, soluble in methanol; its various spectra are reported in (Figs. 3, 4 and 5). Its number-average molecular

weight was 350± 20. The u.v. spectrum suggests a good deal of conjugation, while the i.r. spectrum shows the presence of carbonyl groups (conjugated), furanic structures and probably also olefinic or dihydrofuranic double bonds. The p.m.r. spectrum indicates that this resin still contains aldehidic protons in small amounts, furan-type protons, but also other types of protons giving signals around τ 4 and τ 6.

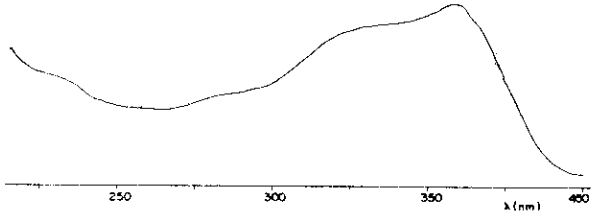


Fig. 3. Ultraviolet and visible spectrum of the methanol-soluble resin. Solvent: ethanol.

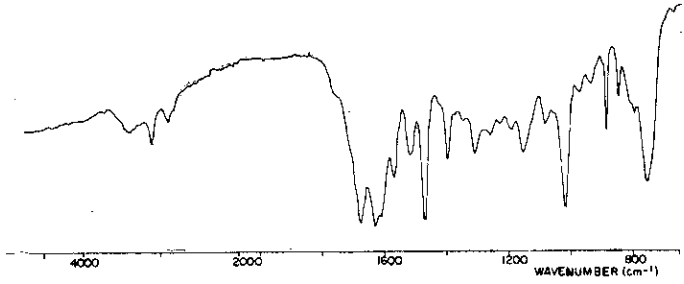


Fig. 4. Infrared spectrum of the methanol-soluble resin (KBr pellet).

2. a black, powdery resin, insoluble in methanol but soluble in methylene chloride, acetone and dimethylsulphoxide. Its spectra are given in Figs. 6, 7 and 8); Mn = 800± 50. The broad, featurless band covering the whole of the u.v. and visible spectrum suggests a high degree of bond delocalization due to resonant structures; the i.r. and p.m.r. spectra are ill-defined, but show features similar to those encountered in the previous resin.

3. a black, insoluble and infusible resin of brittle and powdery consistency. This is the final product of the thermal degradation of furfural which accumulates as a precipitate in the reaction mixture. Its i.r. spectrum is given in (Fig. 9); the same bands as in the two previous resins are present, but with less definition.

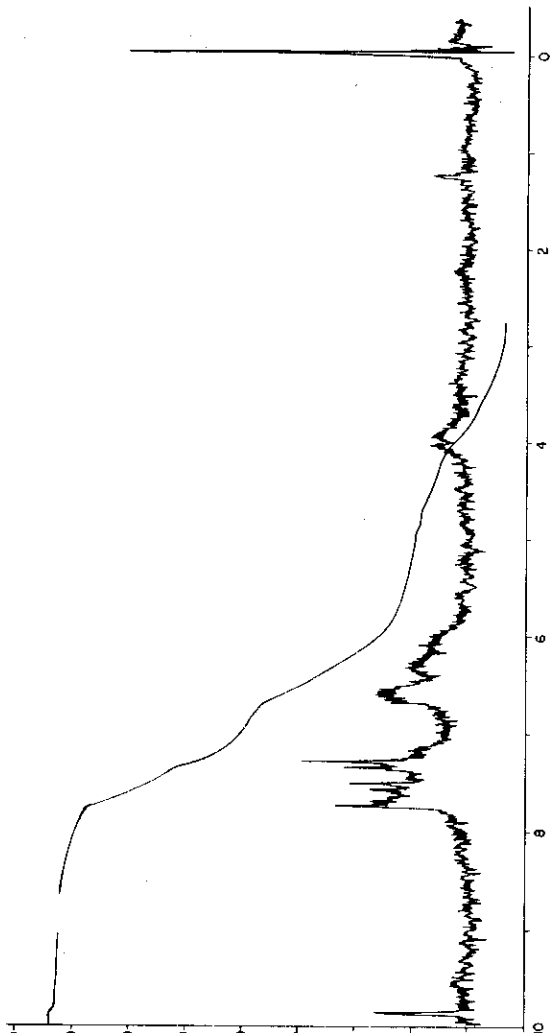


Fig. 5. Proton magnetic resonance spectrum of the methanol-soluble resin (solvent $CDCl_3$, reference: TMS).

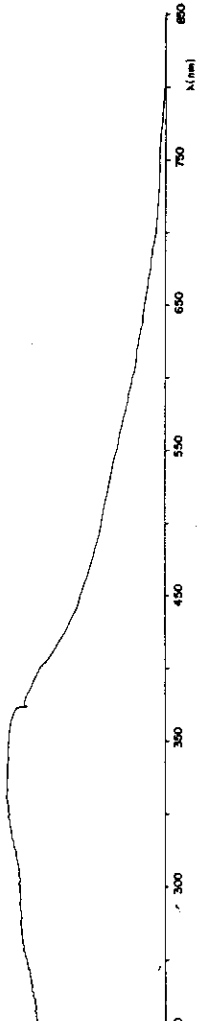


Fig. 6. Ultraviolet and visible spectrum of the dichloromethane-soluble resin Solvent: dichloromethane.

All resins were analysed by e.p.r. and gave intense signals of unpaired electrons with g-values ranging between 2.0074 and 2.0082, i.e. somewhat higher than that of the free electron (2.0023); this indicates delocalization of the electron, probably over a highly conjugated system. The presence of these stabilized free radicals in the resins would explain their deep colour and their broad electronic bands.

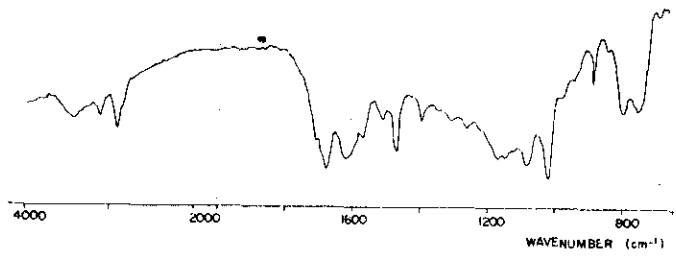


Fig. 7. Infrared spectrum of the dichloromethane-soluble resin (KBr pellet).

These resins were repeatedly submitted to elemental analysis; the results, averaged over several determinations, are given in (Table IV). They all show a loss of water with respect to furfural: about one molecule of water every three molecules of reacted furfural in the case of the orange resin and about one molecule of water for every two molecules of reacted furfural for the black resins. These data agree well with those obtained from the determination of the amount of water produced in the process.

Supplementary Experiments. About 5g of gaseous furfural were treated at 150 ° for several days. Periodically, the gas was allowed to condense and any change in appearence with respect to the original liquid was recorded. Within a couple of days a dark brown resin appeared in spots on the surface of the flask; the condensed liquid turned bright yellow and kept this colour untill the end of the experiment. The resin could not be analysed because it was insoluble and present in minute quantities. Evaporation of the unreacted furfural left an orange, viscous residue which grave i.r. and u.v. spectra similar to those of the methanol-soluble resin described above.

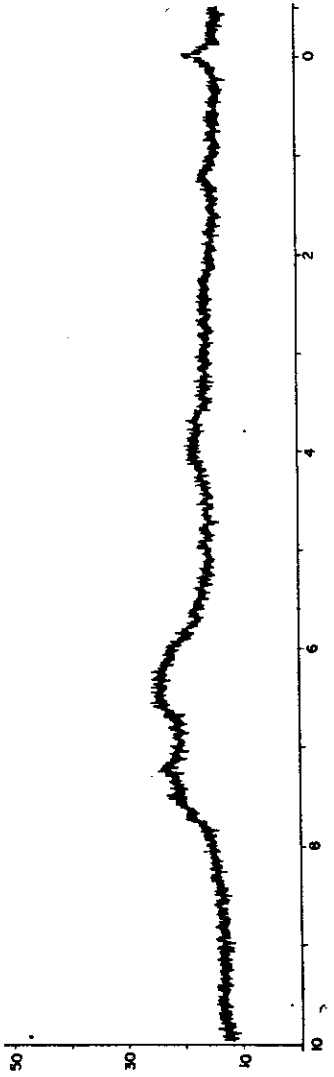


Fig. 8. Proton magnetic resonance spectrum of the dichloromethane-soluble resin (in $CDCl_3$, reference: TMS).

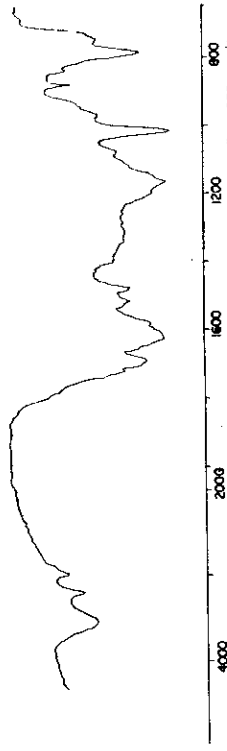


Fig. 9. Infrared spectrum of the insoluble resin (KBr pellet).

TABLE IV

Elemental analysis of the resins (average values)

		% C	% H
Methanol-soluble		65.8	3.9
Dichloromethane-soluble		69.4	4.0
Insoluble		70.3	3.9
Furfural	(calculated)	61.01	4.16
2 Furfural - 1 Water	„	69.0	3.5
3 Furfural - 1 Water	„	66.7	3.7

Various surfaces other than pyrex were tested in liquid-phase experiments at about 150°; the results are summarized below:

1. Treating the pyrex surface with an ammonia solution before evacuation resulted in an appreciable decrease in the rate of resinification.
2. Experiments in soda-glass tubes proceded more slowly then the controls.
3. Experiments in quartz tubes gave higher reaction rates than the controls.
4. Experiments in presence of molecular sieves (Fisher 5A) also gave higher resinification rates than the controls.

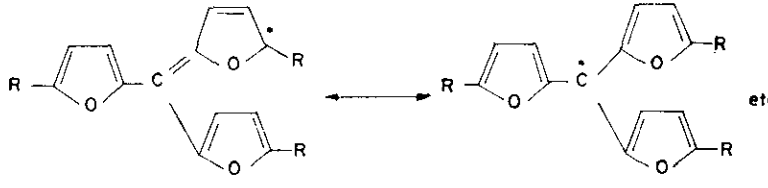
The presence of added water in furfural treated at about 100° made the process slower than the controls.

We also carried out a reaction in which furfural was treated with a drop of 98% sulphuric acid. The resinification proceeded rapidly at room temperature; the products were a black, insoluble resin and an ester. The i.r. spectrum of the resin was quite different from those of the thermal resins; moreover no trace of the two intermediate products reported

above could be found among the products of this reaction. This clearly indicates that the paths of the acid catalyzed resinification of furfural are different from those being studied in the present work.

The soluble resin obtained in one of the thermal reactions was dissolved in freshly-distilled styrene and the solution was sealed-off the line at the same time as a control of pure styrene. The two tubes were placed in a thermostatted bath at 70°; within about 30 hours the control had polymerized to form a near-solid mass, while the resin solution remained virtually free of polymer. Appreciable polymerization begun only after about a week's treatment at 70°. The concentration of the resin in styrene was approximately 300 p.p.m. This strong inhibition is a further demonstration of the presence of stable free radicals in the resin.

The Mechanism. Reaction III, which is probably an equilibrium, in view of the retarding effect of water at 100°, should be considered as the slow step of the overall process and that which is associated with the high activation energy observed. We propose that following the formation of the trifurilic condensate and of the 5-furoylfurfural, these two compounds participate jointly in the resinification. This is born out of the fact that neither of these substances accumulate during the process and that the structural characteristics of both compounds are clearly visible in the spectra of (at least) the orange, methanol-soluble resin. This orange resin would thus be a mixture of low-molecular weight reaction products formed by the addition of these intermediates without appreciables loss of water. Already at this stage, there takes place an abstraction process which leaves unpaired electrons in some of the resin's molecules. This could originate from the removal of a tertiary hydrogen atom from a trifurilic structure producing a highly resonant free radical of the type:



where R indicates a formyl group or larger furanic fragments. These primary resins can react further with the excess furfural or with the

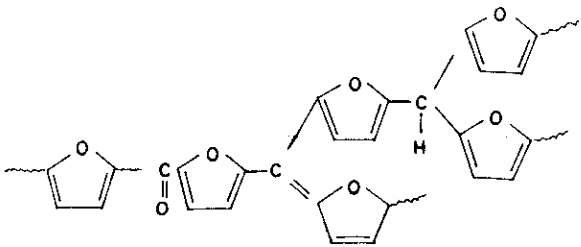
intermediates through condensation and addition steps. Thus the molecular weight increases together with the degree of delocalization of the unpaired electrons (though conjugated structures involving π-electrons and carbonyl groups) and more water is released in the reaction.

The black, soluble resin represents the result of these further steps in the process: broader and bathochromic electronic transitions, higher molecular weights and higher carbon contents.

Finally, due to the large increase of reactive sites in the resin's molecules these reach a prompt reticulation, but maintain their free-radical character: the ultimate product begins to precipitate.

In the first stages of the process one witnesses a build-up of colours which reflects the sequence of events just described leading to the final, insoluble product. Then, a stationary state is reached where the rate of "initiation" (reaction III) is approximately equal to the rate of "termination" (resin precipitation). The "propagation" is here the sequence of reactions making the molecules grow from the trifurilic condensate to the crosslinked product. During the steady-state period of the reaction (plateau in the curves of Fig. 2) the concentration of all soluble products would thus remain small and roughly constant.

It is obviously imposible to give a complete chemical structure for the resins obtained, but they can be reasonably represented by 2,5-disubstituted furan and dihydrofuran rings interjoined by tertiary carbon atoms, carbonyl groups or unsaturated structures; on these molecules unpaired electrons move rather freely through conjugated sequences:



The presence of strong infrared bands typical of the furan ring in the spectra of all the resins obtained suggests that ring opening reactions do not play and important role in this context.

These thermal reactions do not escape ubiquitous surface effect first suspected here from the lack of reproducibility. The experiment with molecular sieves indicates that an increase in the surface-to-volume ratio accelerates the process. Also, the increasing catalytic effect noticed when passing from soda-glass to pyrex to quartz, together with the retarding effect of ammonia washings, suggests that the active sites involved are probably electron-deficient. Defaults in the glass surface, as in seal-off points or in graded seals would be richer in active sites and thus one would explain the first appearance of the insoluble resin in these areas. The present study also provides evidence against the commonly-held view that the thermal and acid-catalysed, resinification of furfural follows a similar mechanism.[10] Despite the similarity in appearance of the two black resins obtained in both processes, the products are quite diferrent, indicanting a different mechanism. Despite the similarity in appearence of the two black resin obtained in both processes, the products are quite different, indicating a different mechanism.

CONCLUSIONS

The thermal treatment of furfural in the temperature range 100 — 250° results in a series of reactions, some catalysed by the vessel's surface, leading to agregation with elimination of water; the final product is a cross-linked resin of complex structure involving delocalized unpaired electrons.

We wish to thank Dr. D. A. Whytock of Essex University for taking the e.p.r. espectra of the resins.

REFERENCES

1. DUNLOP A. P. AND PETERS F. N. The Furans, A.C.S. Monographs Series, 32. New York, 1953.

2. DUNLOP A. P. AND PETERS F. N. *Ind. Eng. Chem. 32,* 1639, 1940.

3. ISACESCU D. A. ET AL. *Bull Soc. Chim. France,* 2171, 1967.

4. ZALUSKI M. C. ET AL. *Bull. Soc. Chim. France,* 1938, 1970.

5. ILLARI G. *Gazz. Chim. Ital.* 77, 389, 1947.

6. NAKAMURA Y. *Kogyo Kagaku Zasshi, 62,* 1179, 1959.

7. RAMANATHAN V. AND LEVINE R. *J. Org. Chem. 27,* 1216, 1962.

8. HEATHCOCK, C. H. ET AL. *J. Het. Chem. 6,* 141, 1969.

9. Unpublished results obtained in our laboratory.

10. Ref. 1, p. 395.