Application of ESR for Coal Pyrolysis and Quench Solvent Evaluation

S.S. Kim, M.L. Jarand and K. Durai-Swamy

Occidental Research Corporation
P.O. Box 19601, Irvine, CA 92713

Introduction

It has long been suspected that radicals play important roles during the pyrolysis of coal and after production of the coal-derived liquids. Our objective is to improve product yields and quality of the coal liquids produced by understanding and controlling free radical chemistry in the pyrolysis processes.

This report describes the experimental results in two parts: Part I, the detection of phenalenyl-like radicals in coal pyrolysis process and Part II, the quench solvent evaluation.

I. Detection of Phenalenyl-Like Radicals

A. Coal Pyrolysis Vapor

Retcofsky et al.[1] recently reported in situ coal pyrolysis experiments in which the solid phase region was studied, but no ESR result was reported on the study of the vapor phase components during coal pyrolysis. In order to detect radicals in the vapor phase during pyrolysis, the experimental apparatus shown in Fig. 1 was used. The coal samples for this experiment were prepared as follows:

> A piece (~5x5x5 cm^3) of Wyodak subbituminous coal was cleaved in a glove box filled with nitrogen to prevent exposure to oxygen. A small piece of coal with all fresh surfaces was selected and ground (~100 microns) in the glove box with mortar and pestle. The coal powder was transferred to a small fused silica tube (2 mm ID, 3 mm OD). The small tube with coal powder was placed in a fused silica tube (3 mm ID, 4 mm OD). The amount of coal used for each sample is 30~40 mgs. Glass wool packing (0.5~1 cm thick) was placed on top of the coal powder which prevents the coal powder from flying to the upper portion of the tube during experiments. The tube was stoppered before removal from the glove box and then quickly connected to a vacuum line. After evacuation overnight, the tube was sealed under vacuum. The length of the tube was made short, compared with the length of the dewar, such that all parts of the tube would be heated during pyrolysis of the coal.

A sample so prepared was placed in the microwave cavity as shown in Fig. 1. The coal was heated by blowing hot air through the dewar using a

commercial electric heater assembly (Wilmad WG-836 and WG-838). With this arrangement, temperatures up to 550°C could be reached within 5 minutes.

For the detection of radicals, a conventional EPR spectrometer (Varian E-109) with X-band rectangular cavity (E-231) was equipped with an "L" shaped water cooled plate attached at the front and bottom sides of the cavity to prevent it from heating by hot air. Signal averaging was done by a Varian E-935 data acquisition system.

Experimental Results and Discussion

When the coal sample was heated to ~510°C, an ESR spectrum with hyperfine structure started to appear. A series of spectra obtained at consecutive times is shown in Fig. 2. Each spectrum shown is an average of 2 scans. When the temperature reached 510°C, an ESR signal (A) with hyperfine structure appeared. Within two minutes another ESR signal (B) appeared at the center of Signal A. The intensity of A signal became steady after 2 min., however, the B signal grew steadily as the pyrolysis proceeded.

When the sample was allowed to cool to ~340°C, the hyperfine structure started to disappear and at room temperature the resulting spectrum was without any hyperfine structure with broader linewidth. At high temperature, the ESR intensity corresponds to ~10^{15} spins. When cooled to room temperature, after the necessary temperature correction with Curie's law, ~30% of the total spin disappeared.

The disappearance of hyperfine structure with overall broadening of the side wing of the central peak strongly suggests that the signal A observed at high temperature was from initial vapor phase radicals that formed during pyrolysis of coal. The gradual growth of B signal after the formation of A suggests that the B radicals could be polymerization products of A. The B radicals probably condense out on the sample tube as they are formed accounting for their loss of hyperfine structure.

A sample tube was opened in the air after the pyrolysis experiment and washed with THF and acetone. A dark brown colored film remained on the inner surface of the tube. The film gave an ESR spectrum which is similar to the room temperature spectrum before opening the tube (see Fig. 2). This film is most likely the speculated polymerized product.

Spectra obtained from three samples are shown with their stick diagrams in Fig. 3. At the bottom of the figure, a calculated ESR spectrum of phenalenyl radicals is shown with corresponding stick diagram for comparison. The simulation was computed on Varian Associates software by using reported[2] proton hyperfine coupling constants, a_1=6.32 G, a_2=1.81 G, and with individual hyperfine linewidth of 1 Gauss and Lorentzian line shape. Broser et al.[3] reported ESR spectra of several alkyl substituted phenalenyl radicals, many of which showed similar overall spectral features. The observed spectra from coal pyrolysis vapor seem to be from a mixture of the alkyl phenalenyl radicals.

The signal B is probably from a polymerization product of the initial phenalenyl-like radicals. Singer and Lewis[4] reported ESR spectra for phenalenyl radical produced by pyrolysis of acenaphthylene in m-quinquephenyl solution at 450°C. They also proposed a possible polymerization scheme of initial acenaphthylene becoming a zethrene-type polycondensed ring structure. As a practical application of this result, one could deduce that if the primary radicals are quenched, stabilized by lighter radicals or hydrogen donors before they polymerize, products with lower molecular weight would result.

The existence of phenalenyl-like radicals in a pyrolysis product of petroleum hydrocarbons was reported by Bennett[5] and Stehling.[6] Thus the detection of phenalenyl radicals in the coal pyrolysis vapor seems to be a reasonable one.

It should be mentioned that the detection of only phenalenyl-like radicals in the pyrolysis vapor does not mean other radicals were not produced in the process. Shorter lived radicals, e.g., alkyl radicals, might have been produced but may not have attained enough concentration to be detected by present method.

B. Coal-Derived Liquids

Coal-derived liquids from the pilot plant pyrolysis reactor 7 were studied by using ESR. The liquids were produced by quenching the pyrolysis vapor with H-donor solvents, e.g., tetralin or hydrogenated creosote oils. Fresh liquids, before exposure to air has occurred, contained phenalenyl radicals together with other stable radicals. The ESR spectrum of fresh coal liquid with calculated phenalenyl spectrum is shown in Fig. 4. The phenalenyl radical signal disappeared when oxygen was bubbled through the liquid. ESR spectrum of the liquid was similar to that of aged coal-derived liquid.

A coal-derived liquid exposed to air was tested with a flow cell reactor originally developed by Livingston et al.[8] At room temperature before heating, the liquid gave an ESR signal (A) (see Fig. 5). When heated at 450°C, phenalenyl-like radical signal (B) appeared on the top of the room temperature coal liquid signal. The difference, (B)-(A), is shown as (C) in Fig. 5. As in the case of coal pyrolysis vapor described earlier, we believe that the signal is a mixture from various alkyl substituted phenalenyl-like radicals.

With another coal-derived liquid, a similar ESR spectrum of phenalenyl-like radicals (D) was observed at 515°C. In the two spectra, C and D in Figure 5, the only difference between the two is the central peaks which are from stable radicals in the coal liquid or polymerized products during pyrolysis. The calculated ESR spectrum of phenalenyl with the reported hyperfine coupling constants is shown at the bottom of the figure.

II. Quench Solvent Evaluation

In the process of coal pyrolysis, various types of radicals are produced. If these radicals are not quenched fast enough, e.g., by H-donor solvents, the radicals may recombine to make polymers. Since the purpose of coal pyrolysis is to make light molecules by breaking bonds of larger molecules, the recombination reaction is highly undesirable. In view of this, the effectiveness of quench solvent in coal pyrolysis is a very important factor for the production of light coal-derived liquids.

There have been studies on evaluation of donor ability of quench solvents, e.g., by Bockrath and Noceti.[9] The usual approach was to generate radicals in various donor solvents and analyze the products by GC/MS technique. Since this method does not give much kinetic information, a solution flow system through which one can directly measure the decay of radicals after introduction of quench solvents was devised.

The flow system of Livingston was modified to study the decay kinetics after injecting donor solvents. Diphenylmethyl radicals were used as a model system to simulate the free radicals generated in the coal liquefaction processes. The diphenylmethyl radicals were generated by pyrolysis (at 440°C, 1300~1400 psi) of 0.02 M 1,1,2,2-tetraphenylethane in 50:50 (volume) benzene-diphenylmethane solution as reported by Livingston.

Experimental Procedure

In the flow system of Livingston et al. a straight fused silica capillary tubing was used as a pyrolysis reactor inside of a microwave cavity. In the present study, the capillary reactor portion was modified to have two inlets and one outlet as shown in Fig. 6. Two capillary tubings (1.2 mm ID x 4.7 mm OD) were joined to accommodate the flow of solution to be pyrolyzed at one branch (1) and the flow of quench solvent at the other branch (2). The capillary reactor was housed inside a fused quartz dewar with the plane of branches 1 and 2 perpendicular to the hot air inlet. Two HPLC pumps (Waters 6000A) were used to pump the liquids to the branches 1 and 2. In this experiment, the solutions once through the flow system were discarded and never recirculated.

Solvents used in the experiment were reagent grade purchased from Aldrich Chemical Co. except hydrophenanthrene. The hydrophenanthrene was made in our laboratory by hydrogenation of phenanthrene under hydrogen pressure at 1500-2800 psi and 370°C with Shell #454 catalyst. After fractional distillation, light yellow liquid portion was collected and used in the quench experiment. The composition of the mixture is shown at the bottom of Table 1.

Both branches of the capillary reactor (see Fig. 6) were heated by blowing electrically heated air through the dewar assembly. In branch 1, radicals were created by pyrolysis of selected model compound solution and then quenched with solvent from branch 2.

The change of radical concentration before and after the introduction of quench solvent was monitored by ESR. In this experiment, ratio of the flow rate of each branch was kept constant, the solution to be pyrolyzed at 1 and the quench solvent at 2 as 4:1 by volume. By varying the flow rate while keeping the ratio constant, the radical concentration was measured as a function of quenching duration, i.e., the period of time needed for the liquid to travel through the 8 cm path from the point of mixing branch 1 and branch 2 to the center of the microwave cavity. To study the kinetics of quenching several sets of flow rates were studied. In each set, the same flow rate was repeated twice, at branch 2, once with benzene and once with the desired quench solvent. In this experiment, benzene was assumed as a non-donor solvent.

To discount the solvent dilution factor and variations in the residence time, the observed ESR signal intensity after mixing with quench solvent (R) was normalized with respect to the case with benzene (R_0). The ratio, R/R_0, was then used as a measure of relative concentration of radicals for a given flow rate.

Experimental Results and Discussion

The relative concentration of diphenylmethyl radical was estimated by measuring the heights of the strongest peaks, I and II (see Fig. 7). Several measurements were repeated and averaged, and an average of peak height I and II was then used as a measure of radical concentration at a given flow rate. This procedure was repeated at each flow rate once with benzene for R_0 and once with quench solvent for R. The ratio, R/R_0, was then plotted in Fig. 8.

The major quench reaction can be viewed as follows:

Radical concentration [R], quench solvent [SH],

$$R\cdot + SH \xrightarrow{k} \begin{cases} RH + S\cdot \\ R\text{-}SH\cdot \end{cases}$$

$$-\frac{d[R]}{dt} = k\,[SH]\,[R] \qquad (1)$$

in which k is a rate constant and t is quenching time. Since [R] <0.02 M, and [R] <<[SH]≈1.5M, we can assume k' = k [SH].

$$-\frac{d[R]}{dt} = k'\,[R] \qquad (2)$$

$$\ln\frac{R}{R_0} = -k'\,(t-t_0) \quad \text{or} \quad \frac{R}{R_0} = \exp\,\{-k'\,(t-t_0)\} \qquad (3)$$

in which t_0 is the time needed for mixing quench solvent with the pyrolyzed solution and k' is the pseudo first order rate constant.

The equation (3) was used to find the best fit values of k' with the experimental $\frac{R}{R_0}$ values for the solvents studied. The results are listed in Table 1.

During the quench experiments, no other radical except the diphenylmethyl radical was detected. It seems that the concentrations of the radicals produced in the quenching process are too low to be detected by ESR. For instance, the concentration of S· radical is expected to be lower than R·, and as soon as the S· radicals are formed, they are engaged in various reaction pathways, such as recombination, disproportionation, etc. and a spread of radical concentrations over various intermediates results. Thus none of the intermediates has high enough concentration to be detected by ESR.

From their end product analysis, Bockrath et al.[8] assigned solvent indices for model hydrogen donor solvents. Using their definition, the ESR result could be accounted as a measure of combination of donor and scavenger effects of quench solvents.

In Table 1, the pseudo first order rate constants, k' derived from ESR results are compared with the solvent indices. The trend seems to agree where the same quench solvent was used. It should be noted that hydrophenanthrene used in this experiment was a mixture rather than a pure compound, 9, 10-dihydrophenanthrene, as used by Bockrath et al.[9]

In a commercial coal pyrolysis process, coal-derived recycle solvent will be preferable and economically more attractive than the above quench solvents. For simulation of the coal-derived recycle solvent, hydrogenated creosote oils were tested using the same flow cell apparatus, to quench diphenylmethyl radicals.

By using this flow cell evaluation method, one can determine the optimum hydrogenation condition of creosote oils for the best quenching effect. The first variable chosen to study was hydrogenation temperature. Samples of creosote oil were hydrogenated at 300, 320, 360 and 400°C. Other conditions were kept constant: reaction time, 0.5 hr; catalyst HDS-9A (American Cynamid); initial hydrogen pressure, 1500 psi. Hydrogenation was done in duplicate 200 gr. batches at each temperature using raw creosote oil in a magnadrive autoclave. Each sample of hydrogenated creosote oil was then stored with molecular sieves (Grade 564, 3A, Davison Chemical, ~50 gr. molecular sieve in ~400 gr.) overnight to remove any water present. The samples were then filtered before use.

The results of quenching experiments are shown in Fig 9. In this series, the creosote oils hydrogenated at 300~320°C seem to give the fastest quenching effect. The mildly hydrogenated creosote oil (300~320°C) was

found to contain ~0.27 mMol/gr of phenolic groups whereas the severely hydrogenated creosote oil (400°C) did not have any detectable amount of phenolic groups. The phenolic groups[10] may play a role as hydrogen shuttlers during the quenching process, thus enhancing the donor ability of the mildly hydrogenated creosote oils.

The modified flow system described in this paper seems to give a convenient and accurate measurement of effectiveness of quench solvents. The quenching experiments were done with only one radical species, namely diphenylmethyl radical. Future experiments will be expanded to other kinds of radicals and with more variety of quench solvents.

Table 1. Quench solvent evaluation. The best fit k' values are compared with the solvent indices of Bockrath et al.[9]

Solvent	k' /sec with t_0=0.72	Solvent Indices [9]		
		Donor Index	Scavenger Index	Combined Index
Cumene	0.10	-	-	-
Mesitylene	0.23	-	-	-
Tetralin	0.54	0.27	0.32	0.59
Hydrophenanthrene#	0.63	0.31*	0.23*	0.53*
Indan	0.98	0.35	0.30	0.65

* with 9, 10-dihydrophenanthrene.

mixtures of vinylnaphthalene, propyldihydronaphthalene, butyldecahydronaphthalene, tetradecahydrophenanthrene, octahydrophenanthrene, dihydrophenanthrene, tetrahydrophenanthrene, phenanthrene, hexahydrophenanthrene, dimethyltetrahydrophenanthrene.

Acknowledgment

This work was done under DOE contract #DE-AC-22-80PC 30264. The authors wish to acknowledge the help of Drs. S. Che, C. B. Chen and R. C. Neuman, Jr. during the course of this work.

References

1. Retcofsky, H. L., Sprecher, R. F., and Hough, M. R. "ESR Spectra of Rapidly Pyrolyzed Coals," Pittsburgh Conference at Atlantic City, NJ, March 1981.

2. Lewis, I. C., and Signer, L. S. J. Phys Chem., 1969, 73, 215.

3. Broser, W., Kurreck, H., Oestreich-Janzen, S., Schlomp, G., Fey, H. J., and Kirste, B. Tetrahedron, 1979, 35, 1159.

4. Singer, L. S. and Lewis, I. C. Carbon, 1964, 2, 115.

5. Bennett, J. E. Proceedings Chem. Soc., 1961, 144.

6. Stehling, F. C., and Bartz, K. W. J. Chem. Phys., 1961, 34, 1076.

7. Durai-Swamy, K., Che, S. C., Chen, C. B., Kim, S. S., Dolbear, G. E. and von Schonfeldt, H., Controlled Flash Pyrolysis, Annual Report to DOE, November 1981.

8. Livingston, R., Zeldes, H. and Conradi, M. S. J. Am. Chem. Soc., 101, 4312 (1979).

9. Bockrath, B. C. and Noceti, R. P. Evaluation of the Donor Ability of Coal Liquefication Solvents, Am. Chem. Soc., Div. of Fuel Chemistry, Preprints of papers presented at Atlanta, GA., March 29-April 3, 1981, Vol. 26, No. 1., p. 94-104.

10. Whitehurst, D. D., Relationships Between the Composition of Recycle Solvents and Coal Liquefaction Behavior, in Proceedings of EPRI Contractor's Conference on Coal Liquefaction, May 1978.

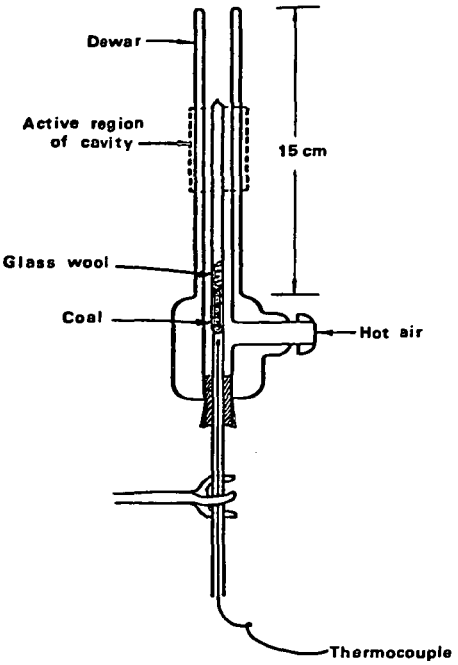

Fig. 1. Experimental apparatus used for detection of radicals from coal pyrolysis vapor.

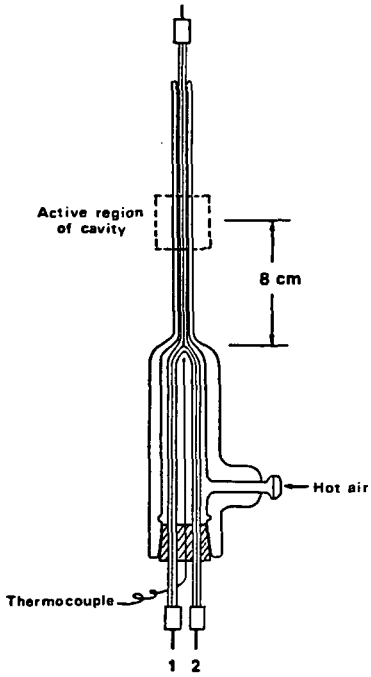

Fig. 6. Apparatus for radical quenching experiments; two inlets were used, 1 for the solution to be pyrolyzed, 2 for the quench solvents.

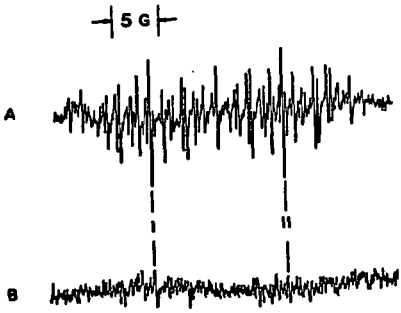

Fig. 7. ESR spectra of diphenylmethyl from 0.02 M tetraphenylethane in equal volume mixture of benzene-diphenylmethane at 440°C and 1300~1400 psi; A. before quenching, B. after mixing with tetralin.
Two peaks, I and II, were used in comparing the degree of quenching with different solvents.

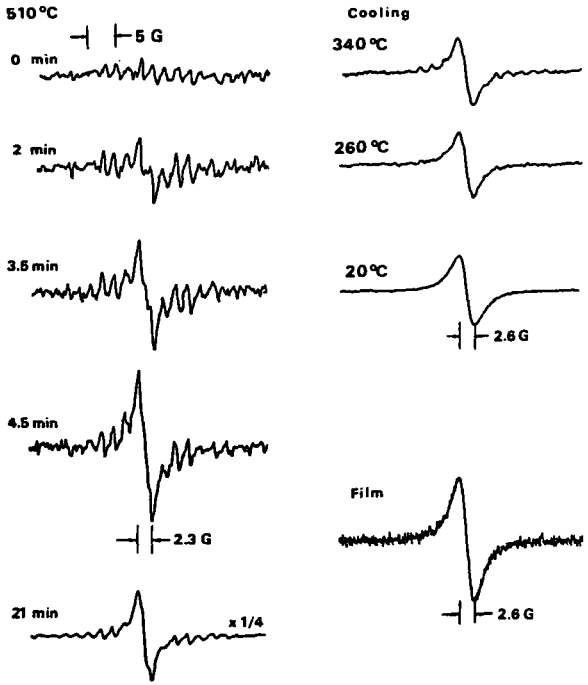

Fig. 2. Time evolution of ESR spectra from Wyodak coal pyrolysis experiment. For heating, the time started after reaching 510°C. The last spectrum is from THF-acetone insoluble film after pyrolysis.

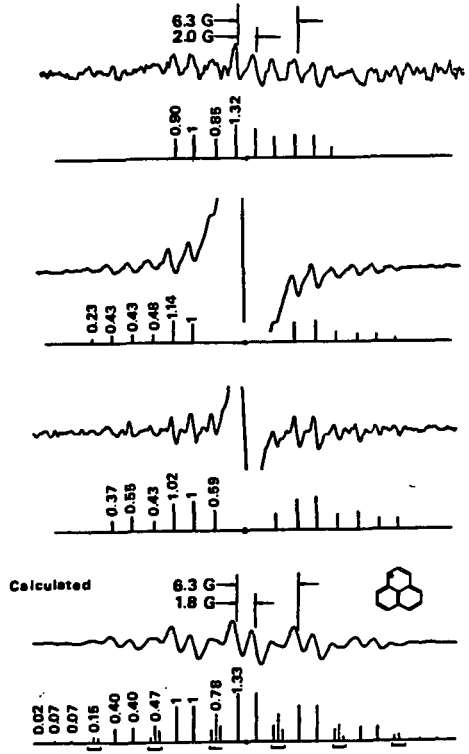

Fig. 3. ESR spectra obtained from three pyrolysis experiments and corresponding stick diagrams are shown. The numbers indicate relative intensities of each hyperfine component averaged for low and high fields. A calculated spectrum is shown at the bottom. In the stick diagram, unresolved neighboring two hyperfine components are represented as sum of the two, with dotted lines.

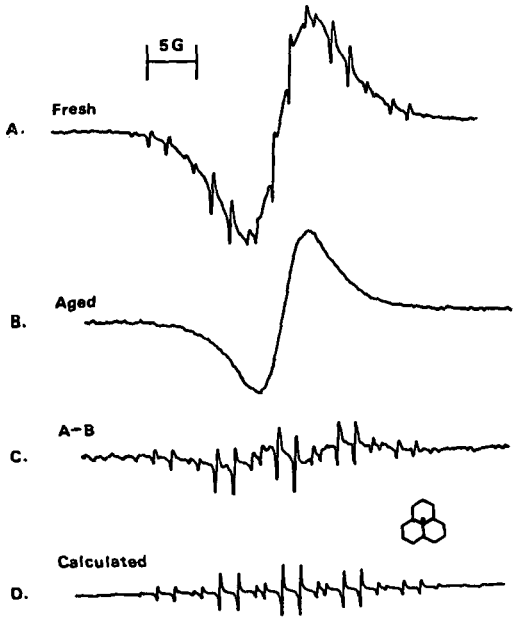

Fig. 4. ESR spectra of coal-derived liquids. The hyperfine structure is identified to that of phenalenyl radical.

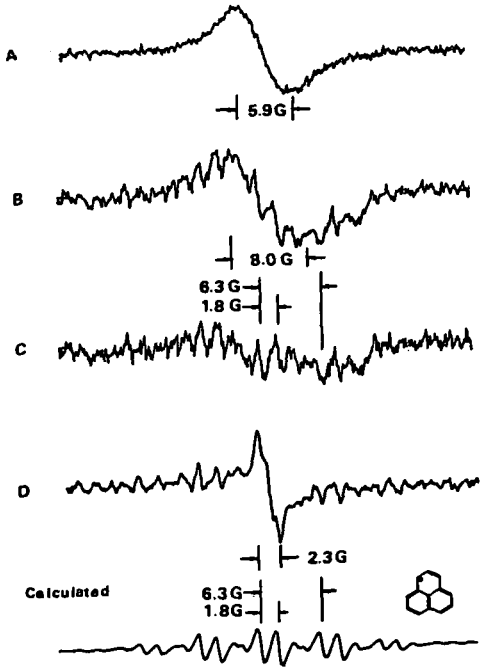

Fig. 5. ESR spectra from thermal up-grading of coal-derived liquid in tetralin. Calculated spectrum of phenalenyl radical is shown at the bottom.

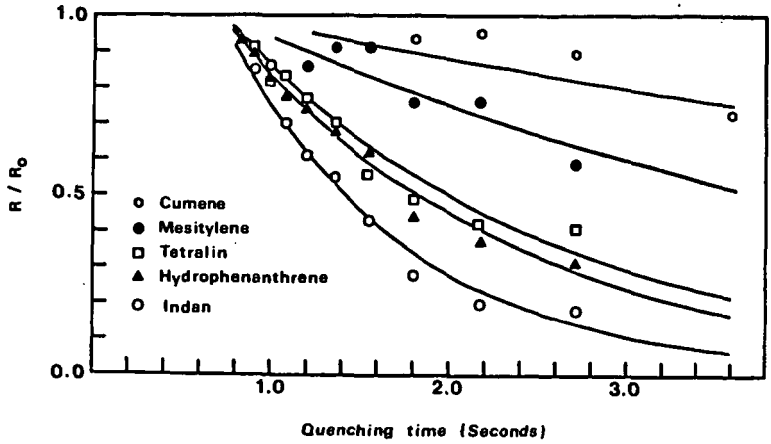

Fig. 8. A plot of R/R_0 as a function of quenching time. The solid curves are calculated values with best fit k'.

R_0 = Radical concentration with benzene at branch 2,

R = Radical concentration with donor solvent at branch 2.

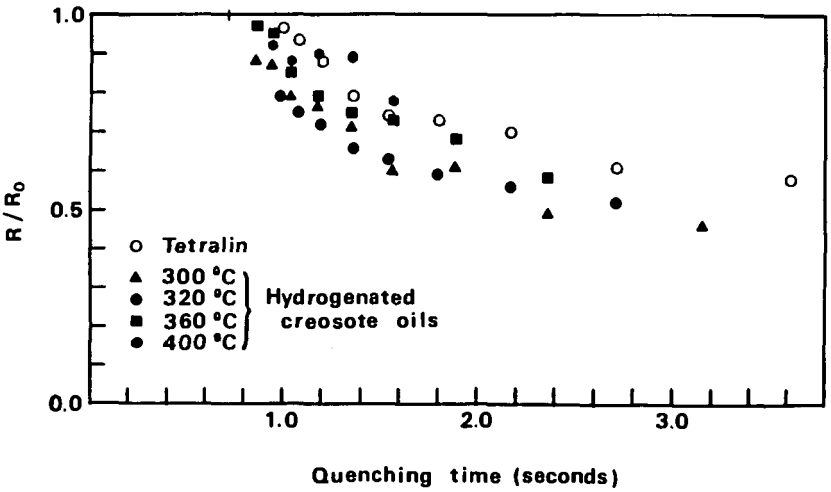

Fig. 9. A plot of R/R_0 vs. quenching time. Hydrogenated creosote oils mixed with benzene (50:50 by volume) were used as solvents for quenching diphenylmethyl radicals.