4,4-d_2-n-Hexyl Mercaptan (VII). 4,4-d_2-Hexyl bromide[6a] (0.5 g) was dissolved in reagent grade acetone and added dropwise to a solution of 0.5 g of potassium ethyl xanthate in acetone. After stirring for 1 hr, the precipitated potassium bromide was filtered, and the product was extracted with chloroform. The xanthate was converted[17] to the mercaptan by heating under reflux with lithium aluminum hydride (0.5 g) in ether for 3 hr. The mercaptan was purified by gas chromatography on polybutylene glycol at 100°.

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[17] C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, *J. Am Chem. Soc.*, 77, 568 (1955).

Organic Polymers. Correlation between Their Structure and Catalytic Activity in Heterogeneous Systems.
II. Models for Dehydrogenation Catalysts

J. Manassen and Sh. Khalif

Contribution from the Plastics Research Laboratory, Polymer Department, The Weizmann Institute of Science, Rehovoth, Israel. *Received November 24, 1965*

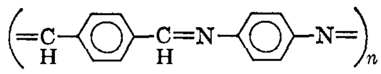
Abstract: The activity of two polymers as heterogeneous catalysts in dehydrogenation reactions in the vapor phase is described. While they have similar stuctures, one is active and the other is not. Both have an extended system of conjugated double bonds, but only the active one has quinoid rings. It is thus shown that it is the latter property that is required for catalytic activity in dehydrogenation. In addition, the concept is tested by using two thermostable organic compounds of known and almost identical structures as catalysts, where likewise the one containing a quinoid unit is active and the other is not. There seems to be a clear correlation between the concentration of free spins as measured by esr and activity toward dehydrogenation, but no correlation can be found with the semiconducting properties of the materials. The importance of these results, which show that the chemical units and not the electronic properties of the solid are responsible for catalytic activity, is discussed, and compared with current theories about the activity of inorganic catalysts.

In a previous publication[1] we reported the catalytic activity of pyrolyzed polyacrylonitrile and polycyanoacetylene in the dehydrogenation of cyclic olefins in the vapor phase. A mechanism was proposed which attributed this activity to conversion of the quinoid annularly condensed ring system of the catalyst into a hydroaromatic one. In the present putlication we intend to prove this concept by describing the catalytic behavior of two poly-Schiff bases, very similar in structure and both containing a polyconjugated system of double bonds. One of them, being polyaromatic, cannot be stabilized by taking up hydrogen and is catalytically inactive. The other one is polyquinoid and is capable of dehydrogenating cyclic olefins in the same way as do pyrolyzed polyacrylonitrile and polycyanoacetylene. To demonstrate that the quinoid unit, and not the extended system of conjugated π electrons, is of overriding importance for the catalytic behavior, results are also given for dehydrogenation reactions over two thermostable organic compounds with a defined structure, which show the same dependence of catalytic behavior on structure.

All dehydrogenations described follow the same pattern in that hydrogen is transferred from the gaseous reactant to the solid, as a result of which the latter is gradually inactivated. A short treatment with air at 150° restores the activity entirely. If the reagent is passed together with air, no deactivation occurs. One may therefore regard this as catalytic activity and not as a reaction between a solid phase and a gaseous reactant only.

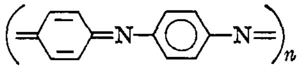
Catalysts

1. AA. Condensation Product of Terephthalaldehyde with *p*-Phenylenediamine. The structure assigned to this product is



and its thermal and electrical properties have been studied.[2,3] The structure sketched above is polyconjugated aromatic. Uptake of hydrogen would disturb the conjugation and is therefore energetically unfavorable. Consequently this polymer can be expected to be inactive as a dehydrogenation catalyst, as is confirmed by experiment.

2. KA. Condensation Product of Cyclohexanedione-1,4 with *p*-Phenylenediamine. A polymer of the structure



has been described in the literature.[4,5] It is commonly thought to be formed by the oxidation of aniline. Because of the uncertainty about the structure of aniline black,[6] however, we looked for an alternative synthesis.

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[1] J. Manassen and J. Wallach, *J. Am. Chem. Soc.*, **87**, 2671 (1965).

[2] Y. U. A. Popov, B. E. Davydov, M. V. Shishkina, and B. A. Krentzel, *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 2014 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (English Transl.), 1855 (1963).

[3] A. V. Topchiev, V. V. Korshak, U. A. Popov, and L. D. Rosenstein, *J. Polymer Sci.*, C4, 1305 (1963).

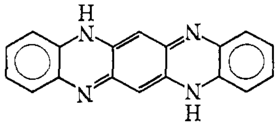
[4] A. A. Berlin, *et al.*, *Dokl. Akad. Nauk SSSR*, **134**, 1123 (1960).

[5] H. A. Pohl and E. H. Engelhardt, *J. Phys. Chem.*, **66**, 2085 (1962).

[6] G. A. Swan and D. G. I. Felton, "The Chemistry of Heterocyclic Compounds," Vol. XI, Weissberger, Ed., Interscience Publishers Inc., New York, N. Y., 1957, p 165.

If cyclohexanedione-1,4 is condensed with *p*-phenylenediamine under exactly the same conditions as were used for catalyst AA, a polymer is obtained, which can easily be dehydrogenated in air to produce the structure sketched above. This compound can take up hydrogen, transferring a quinoid ring into an aromatic one, without disturbing the polyconjugation. Consequently, it can be expected to be active in dehydrogenation as is confirmed by experiment.

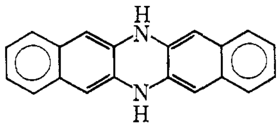
3. **4N. 5,12-Dihydro-5,7,12,14-tetraazapentacene.** The following annularly condensed aromatic structure has been described in the literature.[7]



It is very stable, and when heated in a stream of nitrogen at 350° some of the material sublimes with the gas stream, but it does not decompose.

Therefore its activity as a heterogeneous catalyst can be tested. It is active and can be regenerated like pyrolyzed polyacrylonitrile, polycyanoacetylene, and catalyst KA. This could be expected because uptake of two hydrogen atoms converts a quinoid ring into an aromatic one, without disturbing the conjugation.

4. **2N. 6,13-Dihydro-6,13-diazapentacene.** The thermal stability of the structure



is similar to that of catalyst 4N. It is inactive for dehydrogenation, however, because it cannot take up hydrogen while retaining its conjugation.

5. **PAN. Pyrolyzed Polyacrylonitrile.** Polyacrylonitrile was pyrolyzed as described before[1] at 225° in air and at 350° in a stream of nitrogen.

Results

The experiments were run according to a rigid scheme to ensure that all catalysts underwent the same treatment as far as possible. After pressing, crushing, and sieving, all materials were heated at 350° for 2 hr in a stream of nitrogen of 20 ml/min. After cooling, 4-g portions of each were selected for the reaction.

Table I. Reactions of 1-Methyl-1-ethylcyclohexadiene-3,5 over Different Catalysts[a]

Catalyst	Time passed, hr	Toluene, %	Ethylbenzene, %
KA	1	4	Trace
	4	5	Trace
	1^b	12	Trace
	4^b	11	Trace
AA			No reaction
4N	1	13.5	Trace
	4	2.9	Trace
	1^b	15.1	Trace
	4^b	4.3	Trace
2N			No reaction
PAN	1	1	...
	4	...	...
	1^b	1	...
	4^b	...	...

[a] $T = 350°$. Liquid velocity 4 ml/hr of a 10% solution in pentane; 4 g of catalyst. [b] After regeneration (see text). No methylethylbenzene was formed on any of the catalysts.

Table II. Reactions of *d*-Menthene-1 over Different Catalysts[a]

Catalyst	Time passed, hr	Menthene-2, %	Menthene-3, %	*p*-Cymene, %	Toluene, %	Racemization, %
KA	1	8.8	3.5	9.7	1.3	61.5
	4	6.6	1.3	4.1	0.5	42.3
	1^b	8.0	3.2	10.4	1.6	74.0
	4^b	5.7	1.4	3.5	0.3	56.0
AA			No reaction			
4N	1	3	...	5	1.5	38.0
	4	3	...	1	...	20.0
	1^b	3	...	3.5	1	38.0
	4^b	2	...	...	...	19.0
2N	1	No reaction except for racemization				11.0
	4					11.0
	1^b					24.0
	4^b					15.0
PAN	1	1.5	...	8	1	42.0
	4	2	...	2	...	14.0
	1^b	2	...	5	1	36.0
	4^b	2	...	1	...	13.0

[a] $T = 350°$. Liquid velocity 0.8 ml/hr; 4 g of catalyst. [b] After regeneration (see text). No other materials were formed except some very small quantities of menthene-1,7.

Table III. Reactions of Cyclohexene over Different Catalysts[a]

Catalyst	Time passed, hr	Benzene, %
KA	1	8.6
	4	4.6
	1^b	7.4
	4	5.1
AA	No reaction	
4N	1	2.5
	4	0.6
	1^b	1.9
	4^b	Trace
2N	No reaction	
PAN	1	12.5
	4	4.5
	1^b	14.5
	4^b	4.0

[a] $T = 350°$. Liquid velocity 0.8 ml/hr; 4 g of catalyst. [b] After regeneration (see text). No other materials were formed except for some very small quantities of cyclohexadiene.

For each reactant the following procedure was used. At the start of each run hydrogen was passed at 20 ml/hr at 350° for 10 min to remove the adsorbed oxygen. Then 3–4 ml of the reactant was passed at the reaction temperature. The same catalyst sample was used throughout, and was regenerated between runs by passing air at 150° at 20 ml/min for 2 hr. Each run was performed in duplicate. The reactions were run in the sequence of the tables: 1-methyl-1-ethylcyclohexadiene-3,5 first and limonene last. The reaction products were collected at 0.5-hr intervals and analyzed. In the tables, the results are given only for fractions collected 1 and 4 hr, respectively, after the start of a run. Tables I to IV show the results of the reactions. Butene-1 was run after limonene at 350° with a gas velocity of 6 ml/min, but no appreciable reaction could be detected on either of the catalysts. A clear feature is the inactivity of catalysts AA and 2N in most of the reactions.

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(7) G. M. Badger and R. Pettit, *J. Chem. Soc.*, 3211 (1951).

Table IV. Reactions of Limonene over Different Catalysts[a]

Catalyst	Time passed, hr	Terpinolene, %	α-Terpinene, %	*p*-Cymene, %	*p*-Isopropenyltoluene, %	Racemization, %
KA	1	3.9	2.9	30	1.5	71.0
	4	7.1	3.5	11.1	...	48.7
	1[b]	4.0	4.0	29.9	1.4	59.5
	4[b]	7.2	6.1	15.0	...	54.5
AA	1	No reaction except for racemization				16.5
	4					13.0
	1[b]					67.5
	4[b]					59.4
4N	1	1	Trace	2	2	22
	4	1	Trace	1	Trace	7
	1[b]	1	Trace	2	2	10
	4[b]	1	Trace	0.5	Trace	4
2N	1	1	Trace	1	Trace	5
	4	1	Trace	1	...	0
	1[b]	1	Trace	2	1	12
	4[b]	1	Trace	1	Trace	3
PAN	1	3	Trace	3.5	3	26
	4	2	Trace	2	0.6	11
	1[b]	2	Trace	2.5	2	0
	4[b]	0.5	Trace	1	Trace	5

[a] $T = 300$. Liquid velocity 0.8 ml/hr; 4 g of catalyst. [b] After regeneration (see text). Traces of other products are found, but not the saturated ring compounds.

They lose their inactivity somewhat after many reaction–activation cycles.

Infrared Spectra. Infrared spectra of the materials were recorded, using the potassium bromide pellet technique. No significant difference could be detected before and after the catalytic reactions.

Electrophysical Properties. Table V gives the results of electron spin resonance and conductivity measurements. Because of the heat treatment before and during the reaction, the amount of free spins is higher after reaction for all the compounds, but the difference between active and nonactive materials persists. The resistivity and its activation energy measured for PAN conforms satisfactorily with values given in the literature (computed by extrapolation from ref 8), but the values for AA do not conform with those given in ref 2, where the polymer was synthesized by another method. As can be seen from Table V, no correlation can be found between catalytic activity and either resistivity or its activation energy.

Table V. Electrophysical Properties

Materials	Amount of free spins as measured by esr (arbitrary units) *a*	Amount of free spins as measured by esr (arbitrary units) *b*	Peak width, gauss *a*	Peak width, gauss *b*	Resistance at 21°, ohm cm^{-1}	ΔE, ev[c]
KA	1.0×10^4	3.3×10^4	16.5	12.5	8.4×10^{13}	0.36
4N	7.4×10^3	6.2×10^4	16.5	14.3	4.7×10^{10}	0.34
PAN	3.9×10^3	1.1×10^5	10.7	11.9	4.9×10^{13}	0.28
AA	1.6×10^2	8.4×10^2	12.9	13.0	9.9×10^{11}	0.25
2N	3.8×10	4.3×10^2	15.2	3.76	4.5×10^{11}	0.49

[a] Before reaction and heat treatment. [b] After reaction. [c] See the Experimental Section.

Discussion

In order to explain the catalytic activity of inorganic solids, one can distinguish between two schools of thought. One considers the solid as a matrix for the movement of electrons and holes, and sees the catalytic activity as dependent on the properties of the electrons in the solid as a whole, and as related to such solid-state properties as semiconductivity, which cannot be explained as a property of the separate atoms.[9] Another approach looks at the catalytic activity of the solid in terms of the properties of individual atoms,[10] and in principle one should be able to find parallels between homogeneous and heterogeneous catalytic behavior in this case. It has been amply illustrated that for dehydration reactions of alcohols into olefins for instance, acidity is of overriding importance in homogeneous as well as heterogeneous media, and that many parallels can be found for the behavior of alcohols in both media.[11] Since the appearance of organic semiconductors, some attempts have been made to test their catalytic behavior and to correlate it with their solid-state properties.[12] Electrical and catalytic properties are explained in this case in terms of an extended system of conjugated double bonds, which enables a certain free movement of electrons through the solid, comparable to that in inorganic semiconductors. A different point of view was developed by us in a previous publication,[1] in which a *chemical* property of the composing unit of the polymeric chain was shown to be responsible for the catalytic behavior. It is clear that both approaches in the field of organic catalysts almost parallel those mentioned for inorganic ones. The experimental results given in this paper show clearly that an extended system of conjugated double bonds is not a sufficient condition, whereas the presence of the chemically active unit is a necessity.

Initially the activity of KA, 4N, and PAN are comparable, but that of 4N, which is the monomeric catalyst, decreases rapidly with repetitive reaction–regeneration cycles. This would suggest that extension of the π-electron system does not influence catalytic activity very much, but might be important for giving the molecule sufficient stability. Unfortunately the valence-bond structures cannot give us much information in this respect. Preliminary molecular-orbital calculations by the Hückel method for structures KA and AA do not show extra resonance stabilization with increasing molecular weight, suggesting no stability is gained by extending the π-electron system. We hope to come back to this problem in a subsequent publication.

The chemical behavior of the active catalysts toward the substrates is quite similar. KA seems to be most active for double-bond shifts, as can be seen from Tables II and IV, while PAN is somewhat better at dehydrogenation. Catalyst 4N shows high activity for breaking the C–C bond in methylethylcyclohexadiene, resulting in toluene in Table I. Most surprising is the great discrepancy between the activities of PAN described here and those found previously.[1] The only difference in treatment was the calcination temperature. Heating at 450° as was done previously gives much decomposition, probably with the formation of

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(8) W. D. Brennan, J. J. Brophy. and H. Schonhorn, "Organic Semiconductors," The MacMillan Co., New York, N. Y., 1962, p 159.

(9) G. M. Schwab, *Angew. Chem.*, 75, 149 (1963).

(10) R. S. Nyholm, Proceedings of the 3rd International Congress on Catalysis, North Holland Publishing Co., Amsterdam, 1965 p 25.

(11) H. Pines and J. Manassen, *Advan. Catalysis*, 16, in press.

(12) F. X. de Charentenay, P. Castel, and Ph. Teyssié, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides*, **18**, 1226 (1963).

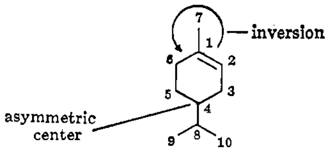

Figure 1.

large cross-linked structures, which are apparently somewhat acidic, resulting in a high activity for double-bond shifts, and even ethyl shifts during the dehydrogenation of 1-methyl-1-ethylcyclohexadiene-3,5. The PAN used in the present experiments was never heated over 350° and showed no activity for double-bond or ethyl shifts. This conforms with electrical measurements, which show great changes to occur at temperatures over 350°.[13]

The mechanism of double-bond shift and dehydrogenation has been discussed previously.[1] The catalysts used in the present work appear to have no acidic sites, and all reactions can be explained on the basis of hydrogen atom transfer. For menthene and limonene, racemization is the preferred reaction, as can be seen from Tables II and IV, and it shows the same dependence on activity of the catalysator as double-bond shifts and dehydrogenation.

Double-bond shift from 1,2 to 1,6 as indicated in Figure 1 would give inversion of configuration. The reason that this shift is so much preferred over the one to the 2,3 position must be sought in the greater stability of the olefin that facilitates hyperconjugation with the methyl group at position 7. Such hyperconjugation may give a stabilization of about 3 kcal.[14] If the double-bond shifts are thermodynamically controlled, a difference of 3 kcal would suffice to explain the preference of the shift from 1,2 to 1,6 over that to the 2,3 position.

It is abundantly clear from our results that the quinoid unit, and not the extended π-electron system, is essential for dehydrogenation, and we have pointed out that it must therefore be possible to find parallels in reactions in solution. Homogeneous dehydrogenation by quinones has been studied extensively,[15] and has been developed into a useful tool in organic synthesis. The new feature of the heterogeneous process is the possibility of regeneration by oxygen, which should in principle be possible also in solution. On the other hand, we have shown with the model compound 1-methyl-1-ethylcyclohexadiene-3,5 that the chemical behavior of commercial chromium oxide or iron oxide catalysts is similar to that of the organic catalysts,[1] which we interpreted as the abstraction of an allylic hydrogen atom by the catalyst. The fact that molecular hydrogen is evolved over the inorganic catalysts and not over the organic ones can best be explained by the strength of the N–H bond formed on reaction over the organic catalyst. Organic catalysts, in which the bond to hydrogen is weak enough to give off molecular hydrogen under dehydrogenation conditions, can probably be synthesized; on the other hand, more and more inorganic catalysts, where oxygen is a necessary partner for dehydrogenation to occur, do appear in the patent literature.[16] Thus parallels can be found between the organic and inorganic dehydrogenation catalysts, and the close, easily explainable parallels between homogeneous and heterogeneous processes in the case of the organic catalysts might also be of help in the approach to the inorganic ones. With the advance of inorganic chemistry, these parallels are indeed found more.[17] The results of Table V can be taken as an example. The clear correlation between dehydrogenation activity and amount of free spins can be expected for the quinoid structures in question, whereas there is no *a priori* reason to expect a correlation with semiconducting properties. The same might be true for dehydrogenation catalysts based on transition metal oxides.

Summarizing, we suggest that results obtained with dehydrogenation reactions over organic catalysts may be applied fruitfully to the problems connected with inorganic ones, and the results published in this paper strongly suggest a mechanism of dehydrogenation because of *chemical* properties of the composing units, *not* of *physical* properties of the solid as a whole.

In subsequent papers of this series we hope to report results obtained with reaction types other than dehydrogenation.

Experimental Section

Condensation of *p*-Phenylenediamine with Terephthalaldehyde. Freshly recrystallized *p*-phenylenediamine (5.4 g) is refluxed with 6.7 g of terephthalaldehyde in a solution of 12 g of anhydrous sodium acetate in 30 ml of glacial acetic acid, in the absence of moisture. The bright yellow polymer precipitates instantaneously and the mixture is refluxed for 30 min. The solid mass is ground in a mortar with water, filtered, and washed thoroughly with water. It is refluxed in 250 ml of dimethylformamide to dissolve unreacted monomer and condensation products of low molecular weight. After refluxing, the mixture is filtered while hot and the residue is ground in a mortar with acetone. Washing with acetone and drying *in vacuo* gives a yield of 5 g of bright yellow polymer.

Condensation of *p*-Phenylenediamine with Cyclohexanedione-1,4. The reaction is executed under exactly the same conditions as described for terephthalaldehyde. A quantity of 5.6 g of cyclohexanedione is used; the condensation is not as fast as with the dialdehyde. The precipitate is red-brown, but changes into brown-yellow after boiling with dimethylformamide. If the polymer is heated for 12 hr at 150° in a thin layer in the presence of air, it turns deep blue and the weight loss agrees with that expected for dehydrogenation.

Both polymers are insoluble in the usual organic solvents; in acids they can be dissolved, but cannot be recovered.

5,12-Dihydro-5,7,12,14-tetraazapentacene. The synthesis is carried out according to the method of Badger and Pettit[7] by condensing 8 g of phenazinediamine-2,3 with 6 g of *o*-phenylenediamine in boiling benzyl alcohol, yield 6 g.

Phenazinediamine-2,3. Freshly recrystallized *o*-phenylenediamine (10.8 g) is dissolved in 500 ml of water. Under ice cooling a filtered solution of 52.5 g of anhydrous ferric chloride in 125 ml of water is added and the mixture is left standing for 12 hr. The dark violet crystals formed are ground with water in a mortar, filtered, and dissolved in 100 ml of boiling water. After being filtered hot and cooled, long needles are formed, which are dissolved in 250 ml of hot water. This solution is added with stirring to a mixture of 50 ml of concentrated aqueous ammonia and 200 ml of water. The orange precipitate of the diamine is free from iron ions as shown by the rhodanide test, yield 6.5 g.

Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.54; H, 4.76; N, 26.70 Found: C, 68.61; H, 4.94; N, 25.71.

6,13-Dihydro-6,13-diazapentacene.[18] In a 100-ml, round-bottom flask 5 g of 2-3-diaminonaphthalene and 5 g of 2,3-dihydroxynaph-

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[13] L. K. H. van Beek, *J. Appl. Polymer Sci.*, **9**, 553 (1965).

[14] P. Coppens, E. Gil-Av, J. Herling, and J. Shabtai, *J. Am. Chem. Soc.*, **87**, 4111 (1965).

[15] L. M. Jackman, *Advan. Org. Chem.*, 2, 329 (1960).

[16] T. G. Jennings and H. H. Voge, U. S. Patent 3,159,688 (1964).

[17] J. Halpern, Proceedings of the 3rd International Congress on Catalysis, North Holland Publishing Co., Amsterdam, 1965, p 146.

[18] O. Hinsberg, *Ann.*, **319**, 259 (1901).

Table VI

Material	Color	Surface area,[c] m^2/g	Formula	Anal, % Found			Calcd			Remarks
				C	H	N	C	H	N	
AA[a]	Yellow	1.2	$C_{134}H_{96}N_{18}O_2$[e]	79.9	4.92	12.51	80.86	4.84	12.69	
AA[b]	Brownish yellow	0.55		78.3	4.51	14.16				
KA[a]	Violet-blue	2.0	$C_{66}H_{44}N_{10}O_2 \cdot 4H_2O$[e,f]	73.15	4.87	12.97	73.20	4.81	12.99	
KA[b]	Brownish blue	1.7		73.19	4.12	13.44				
2N[a]	Yellow	2.2	$C_{20}H_{14}N_2$	85.42	4.87	8.13	85.20	4.96	9.84	Color of DMF soln: blue fluorescent Color of H_2SO_4 soln: red fluorescent
2N[b]	Greenish yellow	1.2		83.74	4.97	9.99				
4N[a]	Metallic violet	17.0	$C_{18}H_{12}N_4$	74.82	4.21	17.26	76.0	4.22	19.78	
4N[b]	Metallic violet	4.6		76.02	4.72	17.60				
PAN[a]	Red-brown	9.5	*d*	57.19	3.13	22.38				
PAN[b]	Dark brown	9.5		64.56	3.17	20.90				

[a] Before reaction and heating. [b] After reactions. [c] The technique of measurement has been described before.[1] [d] As the polymer is known to be partially oxidized, no molecular formula can be given. [e] Approximate molecular weights were computed from the ratios C/H and C/N. [f] Only if some water is assumed to be present, agreement between calculated and experimental values can be found.

thalene are intimately mixed. The mixture is carefully heated to melting over a flame, and heating is continued at 180° in a nitrogen atmosphere for 0.5 hr. The product is ground in a mortar with acetone and filtered. The yellow crystals can be dissolved in 500 ml of dimethylformamide with rigorous exclusion of air. After cooling, long, pale yellow needles that do not melt on heating are obtained. If air is not excluded from the solution, a blue molecular complex is formed, as is also recorded for dihydrophenazine.[19]

Chromatographic Analysis. The reaction products of 1-methyl-1-ethylcyclohexadiene-3,5, cyclohexene, and limonene were analyzed as reported previously.[1] The reaction products of menthene-1 were analyzed over bisethyl hexyltetrachlorophthalate on Chromosorb at 120° and a helium flow of 80 ml/min.

Catalysts. All materials were pressed in 1-g quantities as pellets of 1-in. diameter at a pressure of 4000 psi. The pellets were crushed and sieved between 12–25 mesh sieves. The particles obtained were heated in a 20-ml/min stream of nitrogen at 350° for 2 hr.

Table VI gives some of the physical properties measured. The agreement between experimental and calculated analytical values is not always satisfactory. As we pointed out before,[1] this is a common phenomenon with the intractable materials in question.

Esr Measurements. The materials were introduced into quartz ampoules in powdered form and degassed *in vacuo* at 100° for 1 hr. The spectra were measured on a Varian epr spectrometer V-4502-12 with 9-in. magnet.

Conductivity Measurements. The powdered material (20 mg) was pressed in a die of 1-cm^2 surface under a pressure of 140 atm. On the pellets obtained, electrodes of known surface were painted with silver paint. The conductivities were measured *in vacuo* after degassing at 100° for 1 hr. Voltages ranged from 10 to 100 v and were drawn from a battery, currents were calculated from the drop of voltage over a known resistor, utilizing a Keithley 603 electrometer amplifier. Temperatures ranged from 20 to 75°. Ohm's law was obeyed satisfactorily and in general a plot of log R as a function of $1/T$ gave a straight line. The activation energy was calculated from the slope of the line according to the formula: $R = R_0 \exp(\Delta E/RT)$. No measurements were taken of the catalysts after reaction, because no good pellets could be pressed without using a binder.

Acknowledgments. The authors wish to thank Dr. E. Eschinazi of Givaudan Delawanna Inc. for a generous quantity of pure (+)-1-*p*-menthene and Dr. Ch. Eden, Department of Physical Chemistry, Hebrew University, Jerusalem, for performing the esr measurements.

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(19) See ref 6, p 46.