

*Anal.* Calcd. for  $C_{21}H_{32}O_2$ : C, 79.69; H, 10.13. Found: C, 79.40; H, 10.33.

Reported for the  $\Delta^2$ -derivative<sup>26</sup> m.p. 95–96°;  $[\alpha]_D$  49°;  $\lambda_{max}$  5.75, 6.03, and 14.81  $\mu$ . The  $\Delta^3$ -derivative<sup>27</sup> had m.p. 117–118°;  $[\alpha]_D$  42°;  $\lambda_{max}^{CHCl_3}$  6.07  $\mu$ ;  $\lambda_{max}^{CS_2}$  12.94, 13.60, and 14.90  $\mu$ ; the  $\Delta^4$ -derivative<sup>28</sup> showed

(26) (a) A. Bowers, A. D. Cross, J. A. Edwards, H. Carpio, M. C. Calzada, and E. Denot, *J. Med. Chem.*, **6**, 156 (1963); (b) R. E. Marker, O. Kamm, D. M. Jones, and L. W. Mixon, *J. Am. Chem. Soc.*, **59**, 1363 (1937).

(27) J. McKenna, J. K. Norymberski, and R. D. Stubbs, *J. Chem. Soc.*, 2502 (1959).

m.p. 111–113°,  $[\alpha]_D$  +71°;  $\lambda_{max}^{mineral\ oil}$  5.70, 8.01, 9.53, and 9.74  $\mu$ .

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(28) (a) R. T. Blickenstaff and E. L. Foster, *J. Org. Chem.*, **26**, 5029 (1961); (b) R. E. Marker, E. L. Wittle, and B. F. Tullar, *J. Am. Chem. Soc.*, **62**, 223 (1940).

## Organic Polymers. Correlation between Their Structure and Catalytic Activity in Heterogeneous Systems.

### I. Pyrolyzed Polyacrylonitrile and Polycyanoacetylene

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*Contribution from the Plastics Research Laboratory, Polymer Department, The Weizmann Institute of Science, Rehovoth, Israel. Received November 4, 1964*

*Polyacrylonitrile which is pyrolyzed in the presence of oxygen, and is assumed to contain systems of condensed pyridine rings,<sup>2</sup> is shown to be a strong hydrogen acceptor, being capable of dehydrogenating olefinic compounds in the vapor phase at elevated temperatures. The polymer becomes hydrogenated in the course of the process, and its activity decreases, but it can be restored by air oxidation at 140°. If the process is carried out in the presence of air, the polymer acts as an active dehydrogenation catalyst. It also causes double bond shifts and cis-trans isomerizations in olefinic systems. With the help of model compounds, the mechanism of the hydrogen transfer from substrate to catalyst surface is studied and is shown to occur partly in the form of a hydrogen atom and partly in the form of a hydride ion. The ability of pyrolyzed polymer to be reduced and to be reoxidized under mild conditions is shown to be a function of its proposed chemical structure. Comparison with other carbonaceous materials shows that pyrolyzed polyacrylonitrile and the structurally similar polycyanoacetylene behave in a specific way toward olefinic hydrocarbons. It is also shown, by using model compounds, that the transfer of an allylic hydrogen to several commercial dehydrogenation catalysts occurs exclusively in the form of a hydrogen atom.*

#### Introduction

In recent years many polymers have been synthesized, stable at high temperatures,<sup>3a</sup> which show interesting physical properties such as semiconductivity and give significant signals in electron spin resonance spec-

troscopy.<sup>3b</sup> Their catalytic activity in a heterogeneous system has been studied for the decomposition of hydrogen peroxide<sup>4</sup> and formic acid,<sup>5,6</sup> autoxidations,<sup>6,7</sup> dehydrogenations and dehydrations,<sup>6,8,9</sup> and the decomposition of hydrazine and nitrogen oxide.<sup>6,8,-</sup> The purpose of most of these studies has been to find a correlation between physical properties and catalytic activity, which has also been widely attempted for inorganic catalysts.<sup>10</sup>

In the present paper the first results are described of a study, whose purpose can be said to be threefold: (1) to find a correlation between catalytic activity and the chemical structure of the polymer, which might throw more light on the phenomenon of heterogeneous catalysis in general; (2) to obtain information about the structure of the polymer from its behavior with respect to chemical reactions; (3) to find ways of synthesizing specific organic catalysts which might resemble those used in industrial, high-temperature applications as well as those encountered in biochemical systems.

Pyrolyzed polyacrylonitrile has been chosen as the first polymer because its structure has been studied to some extent.<sup>2</sup>

As the structure proposed for pyrolyzed polyacrylonitrile can be synthesized in principle by the polymerization and heat treatment of cyanoacetylene in the absence of air, this monomer has been polymerized

(1) This work has been done as partial fulfillment for the Ph.D. Thesis of J. Wallach.

(2) (a) R. T. Conley and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 1757 (1963); (b) T. Takata, J. Hiroi, and M. Taniyama, *J. Polymer Sci.*, **2**, 1567 (1964); (c) N. Grassie and J. N. Hay, *ibid.*, **56**, 189 (1962).

(3) (a) G. Lefebvre, *Rev. Inst. Franc. Petrol. Ann. Combust. Liquides*, **18**, 1192 (1963); (b) F. X. de Charentenay, P. Castel, and Ph. Teyssié, *ibid.*, **18**, 1226 (1963).

(4) (a) A. V. Topchiev, M. A. Geiderikh, *et al.*, *Dokl. Akad. Nauk SSSR*, **128**, 312 (1959); (b) A. A. Berlin, L. A. Blyumefeld, and N. N. Semenov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **9**, 1689 (1959).

(5) E. S. Dokukina, S. Z. Roginski, M. M. Sakharov, *et al.*, *Dokl. Akad. Nauk SSSR*, **137**, 893, 1404 (1961).

(6) N. R. Kayer, and I. U. Astafieff, *Kinetika i Kataliz*, **3**, 364 (1962).

(7) S. Z. Roginskii, A. A. Berlin, L. M. Kutseva, *et al.*, *ibid.*, **148**, 118 (1963).

(8) J. Gallard, M. Nechtschein, M. Soutif, *et al.*, *Bull. soc. chim. France*, 2204 (1963).

(9) J. Gallard, Th. Laederlich, M. Nechtschein, *et al.*, Proceedings of the Third Conference on Heterogeneous Catalysis, Amsterdam, 1964.

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

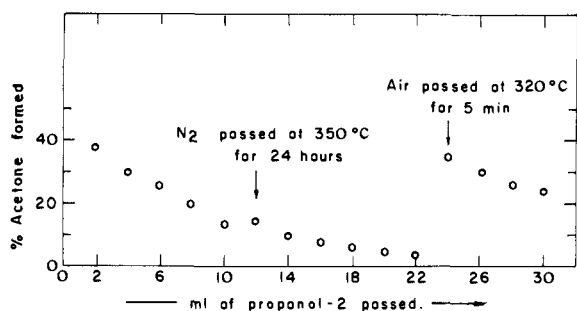


Figure 1. Deactivation of pyrolyzed polyacrylonitrile during dehydrogenation of propanol-2. Activity is restored rapidly by air oxidation.

and the catalytic properties of the pyrolyzed polymer have been checked.

## Results

1. *Dehydrogenation. A. Alcohols.* If acrylonitrile is polymerized, pyrolyzed at 250° in air, and pressed at 8000 p.s.i., black pellets are obtained, which can be calcined at 450° in a nitrogen stream. A catalyst is thus obtained which converts propanol-2 into acetone and cyclohexanol into cyclohexanone in the vapor phase at 250°.

Apparently it acts as a conventional dehydrogenation catalyst with the important difference that *no gaseous hydrogen is evolved*.

As no other reaction products are formed (except those of a concurrent dehydration reaction), the hydrogen is either physically adsorbed or chemically bound to the catalyst. Prolonged heating in a nitrogen stream does not reactivate the surface. A short treatment with air, on the other hand, at temperatures as low as 140°, gives total restoration of the original dehydrogenation activity. Water is produced simultaneously. (See Figure 1.) Consequently the conclusion can be drawn that the hydrogen is chemically bound to the surface but can be removed by oxygen under very mild conditions.

B. *Cyclohexene.* Alcohols can only be studied under relatively low temperatures as they tend to decompose thermally. Cyclohexene, on the other hand, is thermally stable at temperatures up to 450°, but easily disproportionates to cyclohexane and benzene in the presence of palladium.<sup>11</sup> If passed over 5 g. of pyrolyzed polyacrylonitrile at 350° at a liquid velocity of 0.8 ml./hr., about 50% is converted into benzene, but neither cyclohexane nor gaseous hydrogen is formed. The catalyst activity decreases rapidly, but can be restored under exactly the same conditions as described in the previous section. If cyclohexene is passed over the catalyst together with air, conversions into benzene of more than 50% per pass are easily obtained and no rapid deactivation occurs. The polymer acts in this case as a real dehydrogenation catalyst. If the reaction is performed in an empty reactor or over glass beads, peroxidation occurs and only an intractable brown reaction mixture is formed.

Treatment of the catalyst with gaseous hydrogen for 0.5 hr. at 350° does not cause deactivation, which shows

(11) G. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954).

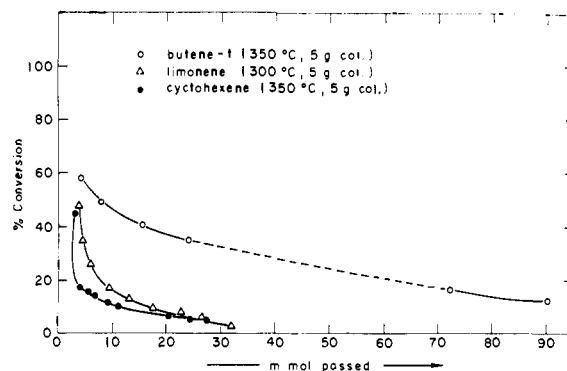


Figure 2. Deactivation of pyrolyzed polyacrylonitrile during dehydrogenation of limonene and cyclohexene, compared with that caused by the isomerization of butene-1.

that gaseous hydrogen is not an intermediate and that a direct transfer occurs from substrate to surface.

In Table I the behavior of pyrolyzed polyacrylonitrile toward cyclohexene is compared to that of other materials. The absence of cyclohexane in the case of polyacrylonitrile and polycyanoacetylene is striking.

2. *Isomerization. Butene-1 and Butene-2.* Pyrolyzed polyacrylonitrile causes double-bond shifts as well as *cis-trans* isomerizations in olefinic systems, and in Tables II and III the results are given of a study about the behavior of the *n*-butenes.

Under the conditions used, no dehydrogenation occurs (no butadiene being found), so theoretically the activity of the catalyst should remain constant. In Figure 2 conversions are plotted as a function of amount of millimoles of limonene, cyclohexene, or butene-1 passed over the catalyst. As can be seen, the decrease in activity with regard to the dehydrogenation of cyclohexene and limonene is greater than for the isomerization of butene-1, as could be expected if transfer of hydrogen deactivates the catalyst toward dehydrogenation. The decrease found with the isomerization of butene-1 is probably due to trivial causes like polymer and coke formation on the surface of the catalyst.

At the very beginning of the reaction on a freshly regenerated catalyst, some propene is formed. As traces of water are formed simultaneously, its formation might be best explained by decomposition of free radicals, obtained from a reaction with oxygen atoms chemisorbed on the surface after regeneration of the catalyst.

3. *Competitive Isomerization and Dehydrogenation. A. Limonene.* The optically active limonene molecule undergoes double-bond shifts as well as dehydrogenation, and Scheme I illustrates what we might expect, based on the results obtained with cyclohexene and the butenes. The experimental results are given in Table IV.

B. *5-Ethyl-5-methyl-1,3-cyclohexadiene.* The hydrogen transfer from substrate to surface, in which, as we have seen, molecular hydrogen is not an intermediate, can in principle be in the form of either a proton, an atom, or a hydride ion.

In scheme II is shown how a model compound (5-ethyl-5-methyl-1,3-cyclohexadiene) enables distinction between the three possibilities. If a hydride ion is

**Table I.** Reactions of Cyclohexene over Various Materials at 350°

Material	Wt. of material used in reaction, g.	Surface area, m. <sup>2</sup> /g.	Liquid feed, ml./hr.	Cyclohexene passed, ml.	Products, %		
					Cyclohexane	Benzene	Others
Animal charcoal	20	128	0.8	1	20	27	...
Coconut charcoal	12.5	1030	0.8	2	63	35	...
Graphite	13	20	0.8	0.6	35	3	20
Graphite <sup>a</sup>	13	20	0.8	0.6	9	12	13
				1.0	9	7.5	12
				1.4	8	2	11
Polyacrylonitrile <sup>a</sup>	13	18	0.8	0.5	...	33	...
				0.9	...	19	...
				1.7	...	10	...
Polycyanoacetylene	0.25	36	40 <sup>c</sup>	20 <sup>d</sup>	...	4	3 <sup>b</sup>
Boiling stones <sup>e</sup>	5	196	0.8	1	...	...	...

<sup>a</sup> Air passed at 200° for 15 min. and afterwards hydrogen at 400° for 15 min. <sup>b</sup> The product in question was cyclohexadiene, the precursor in dehydrogenation to benzene. <sup>c</sup> μl./hr. <sup>d</sup> μl. <sup>e</sup> Fisher "boileezers."

**Table II.** The Isomerization of Butene-1 over Pyrolyzed Polyacrylonitrile<sup>a</sup>

Butene passed, ml.	trans-Butene-2, %								cis-Butene-2, %								Ratio of trans to total butene-2								
	300°		350°		400°		450°		300°		350°		400°		450°		300°		350°		400°		450°		
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	
90		27						22									0.64	0.55	0.63		0.62			0.61	
180	11	24	35	34	9	23	27	35	0.55									0.51	0.63		0.56			0.58	
360	9	21	28	29	10	20	24	23	0.47									0.51			9.54			0.56	
540	6	17	22	25	7	18	21	20	0.46									0.48			0.51			0.55	
720	7		20	22	7		19	19	0.50												0.51			0.54	
900	5		18	20	6		16	17	0.45												0.53			0.54	
1080	4			20	4			18	0.50															0.53	
1260				20				17																	0.54
1620		8.5	14	16		8.5	12.5	14										0.50			0.53			0.53	
1980		6.5	12	15		6.5	10	13										0.50			0.53			0.54	

<sup>a</sup> At gas feed of 6 ml./min.; 5 g. of polymer used. The thermodynamical quantities have been calculated by interpolation from data by J. E. Kilpatrick, E. J. Prosen, U. S. Pilzer, and F. O. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 559 (1948).

**Table III.** The Isomerization of trans-Butene-2 over Pyrolyzed Polyacrylonitrile<sup>a</sup>

trans-Butene-2 passed, ml.	cis-Butene-2, %				Butene-1, %				Ratio of cis-butene-2 to butene-1						
	300°		350°		300°		350°		300°		350°		350°		
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	
360	11		22		5		15		2.2		1.5		1.5		1.2
540	10				4				2.5						
720			14				11						1.3		
900	7				3				2.3						
1080			10:5				8						1.3		
1260	6.5				2.5				2.6						
1440			9.5				7						1.35		
1800			9.5				6.5						1.45		

<sup>a</sup> At gas feed of 6 ml./min.; 5 g. of polymer used. See Table II, footnote a.

**Table IV.** The Isomerization and Dehydrogenation of (-)-Limonene over Pyrolyzed Acrylonitrile<sup>a</sup>

Limonene passed, ml.	Product, %				Racemization of limonene, %
	Terpinolene	α-Terpinene	p-Cymene	Iso-propenyl toluene	
0.6	6	3	28	19	72
0.8	7	3	20	15	55
1	7	3	14	12	40
1.4	7	2.5	9	8	43
2.2	6.5	2	8	5	22
3	6	Trace	7	3	6
3.8	5	Trace	5	2.5	1
4.6	5	Trace	4	2	1
5.4	4	Trace	3	Trace	..

<sup>a</sup> At liquid feed of 0.8 ml./hr. and 300°; 5 g. of polymer used. Other isomerization products, including menthenes and menthanes, were present in negligible quantities. In absence of polymer, no reaction occurred.

abstracted, an electron sextet will develop at C-2. Such a system stabilizes itself most easily by gaining aromaticity through a Wagner-Meerwein shift and subsequent proton loss.<sup>12</sup> So the expected product is *o*-ethyltoluene.

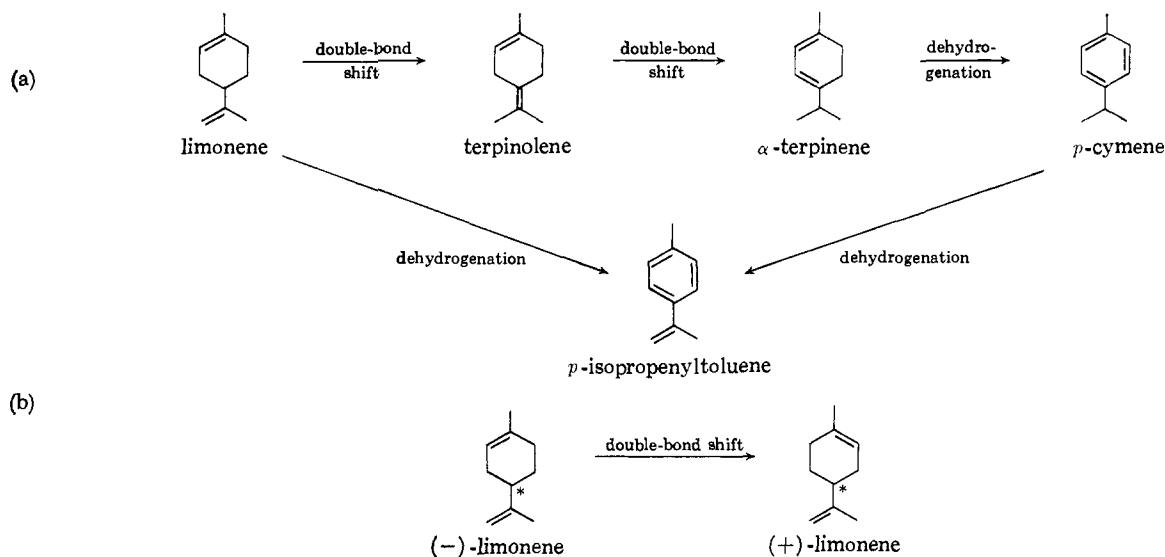
Migrations of this kind in the heterogeneous dehydrogenation of cyclohexenes containing a geminal carbon atom have been found by Pines, *et al.*, under acidic conditions.<sup>13</sup> If a hydrogen atom is abstracted, an unpaired electron will be located at C-2. As 1,2-shifts of methyl or ethyl groups are practically unknown in systems of this kind,<sup>14</sup> stabilization by aromatization

(12) Y. Pocker, "Molecular Rearrangements," Interscience Publishers, Inc., New York, N. Y., 1964, p. 1.

(13) H. Pines, E. F. Jenkins and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 6227 (1953).

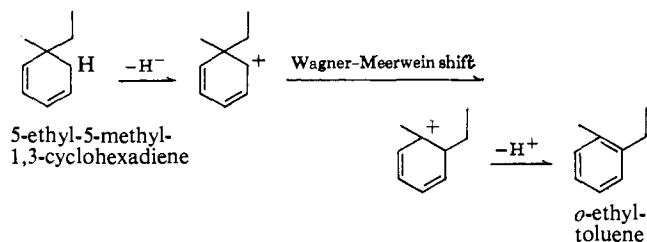
(14) C. Walling, ref. 12, p. 407.

Scheme I

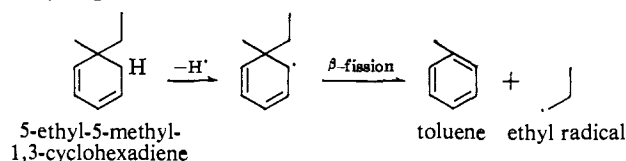


Scheme II

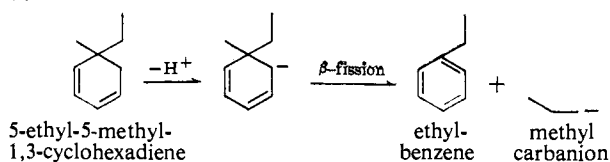
(a) Hydride ion abstraction



(b) Hydrogen atom abstraction



(c) Proton abstraction



is brought about by fission of the C-C bond in a  $\beta$ -position with respect to the unpaired electron.<sup>15</sup>

As an ethyl radical is known to be more stable than a methyl radical,<sup>15</sup> it will leave preferentially and toluene will be the main product. Pines and co-workers showed that under strongly basic (*i.e.*, proton abstracting), conditions it is the methyl which is split off, giving ethylbenzene as the main product.<sup>16</sup> The reason is that the methyl carbanion is more stable than the ethyl carbanion and thus is split off preferentially.

In Table V the product distribution of 5-ethyl-5-methyl-1,3-cyclohexadiene on reaction over different catalysts is given and its usefulness as a tool to dis-

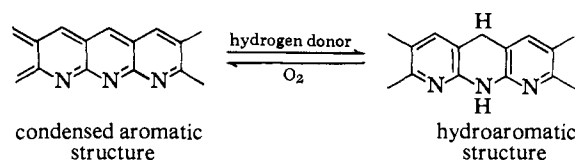
tinguish between hydride and atom abstraction is clear.

4. *Autoxidation. Cumene.* Polymers with a chain of conjugated double bonds or rings are reported to be good catalysts for autoxidation reactions.<sup>7</sup> Although autoxidations and dehydrogenations are closely related mechanistically, pyrolyzed polyacrylonitrile, in its reduced as well as in its oxidized form, is shown to inhibit the autoxidation of cumene instead of accelerating it. This is illustrated in Figure 3.

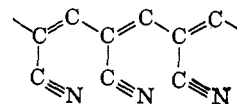
Discussion

From Tables I and V it can be seen that pyrolyzed polyacrylonitrile as well as polycyanoacetylene is capable of dehydrogenating cyclic olefins, without simultaneous formation of saturated hydrocarbons or gaseous hydrogen. This is contrary to the behavior of other carbonaceous materials and palladium which cause disproportionation, or of commercial dehydrogenation catalysts which produce gaseous hydrogen. In terms of reaction mechanism, this means that the materials in question are good hydrogen acceptors. The hydrogen is retained chemically bound until it is removed during regeneration of the catalyst by oxygen under very mild conditions.

This property can best be explained by considering the structure of annularly condensed pyridine rings, which is assumed for pyrolyzed polyacrylonitrile<sup>2</sup> and which gains aromaticity by being hydrogenated.



The nonpyrolyzed polymer of cyanoacetylene is black, which indicates a highly conjugated structure. It shows a strong signal for C $\equiv$ N groups in the infrared, which suggests the following structure. On pyrolysis



(15) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

(16) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, **78**, 5950 (1956).

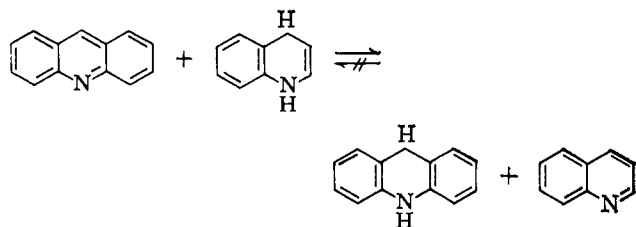
Table V. Reaction of 5-Ethyl-5-methyl-1,3-cyclohexadiene over Different Catalysts

Catalyst	Wt. of catalyst, g.	Surface area, m. <sup>2</sup> /g.	Temp., °C.	Liquid feed, ml./hr.	Products, %				Ratio of toluene to <i>o</i> -ethyl-toluene
					Toluene	<i>o</i> -Ethyl-toluene	Ethyl-benzene	Others	
Acid-washed alumina (Merck)	1	233	300	8	..	53	..	32	Small
Polyacrylonitrile	5	18	350	4 <sup>a</sup>	11	5	Trace	..	2.2
Iron catalyst (Harshaw, No. Fe-0301)	6	61	300	8	45	3	8	5	15
Chromia alumina (Harshaw, No. CR-1404)	3	125	300	8	77	4	10	4	19
Polycyanoacetylene	5 <sup>b</sup>	206	350	4 <sup>a</sup>	26	Trace	2	18	Great
Boiling stones (Fisher "boileezers")	5	196	350	4 <sup>a</sup>	...	...	...	25	...

<sup>a</sup> A 10% solution of the diene in *n*-pentane. <sup>b</sup> Five grams of "boileezers" impregnated with 0.3 g. of the polymer.

the material does not undergo any visible change, but the infrared absorption of C≡N groups disappears. This suggests an internal condensation reaction leading to the same structural element of annularly condensed pyridine rings as assumed for polyacrylonitrile. Although it is very difficult to prove aromatization of this kind it has been proposed for pyrolyzed polyacrylonitrile by different authors.<sup>2</sup> The catalytic activity of polyacrylonitrile and polycyanoacetylene stands apart from that exhibited by other pyrolyzed organic materials, and the best explanation is the condensed aromatic structure which can be assumed to be present in both of them and not in the other materials. Work is in progress to elucidate the structure of polycyanoacetylene and to test the catalytic activity of other compounds containing a condensed aromatic structure. Several arguments can be given in favor of such a structural element performing the reactions in question.

Braude and co-workers, in their extensive studies on hydrogen transfer, described how dihydroquinoline can be dehydrogenated by acridine, but the reverse reaction does not occur.<sup>17</sup> They formulated the



principle, that the higher the annelation of a system of condensed heterocyclic aromatic rings, the poorer will be the H-donor properties.

It is also well known that annularly condensed aromatic molecules become less and less stable with an increasing number of rings. The hydrogenated compounds, on the other hand, gain in stability.<sup>18</sup> This may explain why a macromolecular compound containing such a structure is a good acceptor and a poor donor. The transition of the hydroaromatic into the aromatic compound by air oxidation is known to occur with acridine<sup>19</sup> and has also been described by Takata for model compounds of condensed pyridine rings.<sup>20</sup>

(17) E. A. Braude, J. Hanna, and S. R. Linstead, *J. Chem. Soc.*, 3268 (1960).

(18) E. Clar, "Aromatische Kohlenwasserstoff," Springer-Verlag, Berlin, 1952.

(19) S. M. Badger, "The Chemistry of Heterocyclic Compounds," Academic Press Inc., New York, N. Y., 1961, p. 354.

It has been shown in the Results section that with the aid of 5-ethyl-5-methyl-1,3-cyclohexadiene a distinction can be made between atom and hydride transfer. From Table V can be seen that the behavior of polyacrylonitrile is intermediate between that of the commercial dehydrogenation catalysts (which abstract H atoms) and acidic alumina (a hydride abstractor). Polycyanoacetylene shows only H-atom abstraction.

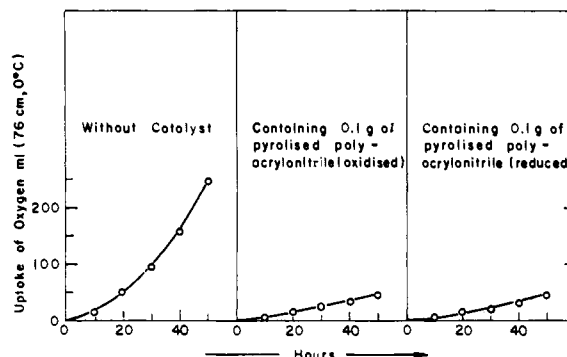
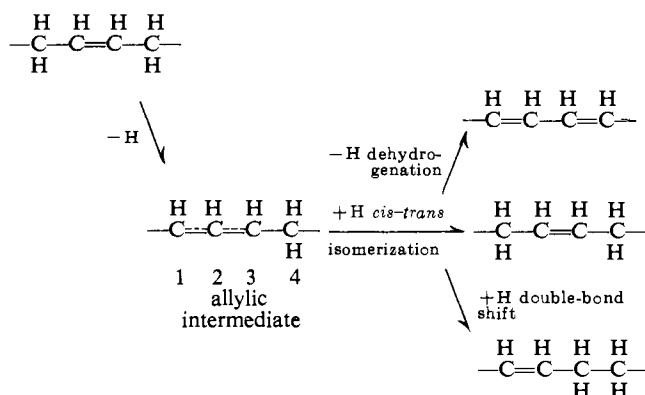


Figure 3. Autoxidation of cumene at 90°. Pyrolyzed polyacrylonitrile in the oxidized as well as reduced form inhibits the reaction.

The quinoid structure found in a linear polyaromatic system can be expected to lead to atom transfer only as is confirmed in the case of polycyanoacetylene. One would suspect, therefore, that the hydride transfer to polyacrylonitrile originates from another structural element. An indication in this direction is the fact that the 1,2-shift of ethylmethylcyclohexadiene in its reaction over polyacrylonitrile can be greatly enhanced by treating the catalyst with dimethyl sulfoxide at 350°. The acidic (hydride-abstracting) sites on pyrolyzed polyacrylonitrile might be responsible for its activity toward the dehydration of alcohols.<sup>6,8,9</sup>

In terms of the reaction mechanism as outlined above, we can discuss the reactions of the *n*-butenes and limonene over pyrolyzed polyacrylonitrile. The absence of saturated compounds in the reaction products makes a transfer of hydrogen from the catalyst surface to the double bond unlikely, and we have to consider as the first step in dehydrogenation as well as in isomerization the abstraction of an allylic hydrogen. It is impossible to conclude from our experiments whether an allylic intermediate exists or whether a concerted re-

(20) T. Takata, *Bull. Chem. Soc. Japan*, 35, 1438 (1962).



action sequence occurs. It is more convenient, however, to discuss the mechanism in terms of an allylic intermediate.

The double-bond shift of butene-1 has been studied over a number of catalysts. In general, the ratio of *cis*- to *trans*-butene-2 is greater than one over acidic as well as basic catalysts, although the *trans* is the more stable form.<sup>21</sup> Although several theories have been put forward, this phenomenon seems to be as yet unexplained. If the isomerization is caused by iodine atoms, *cis*- and *trans*-butene-2 are formed at about the same initial rate.<sup>22</sup>

From Table II we see that, at all temperatures studied, *cis*- and *trans*-butene-2 are formed at about the same rate. In terms of the allylic intermediate, this means that its *cis* and *trans* configurations are in rapid equilibrium and that the transition states for their reaction into the isomerized olefin do resemble more the intermediate than the product.

In Table III the products are given when *trans*-butene-2 is the reactant. Double bond shift gives butene-1; *cis-trans* isomerization gives *cis*-butene-2. The ratio of *cis*-butene-2 to butene-1 is higher than that calculated from the thermodynamic stability of the products, but the effect is less pronounced at higher temperatures. *cis-trans* isomerization might conceivably occur by reversible addition to the double bond; such a reaction, however, would be expected to be more pronounced at higher temperatures.

We have seen from Table II that the *cis* and *trans* configurations of the allylic intermediate can be considered to be in rapid equilibrium. If butene-2 is the reactant, addition of hydrogen to C-1 of the allylic intermediate will give *cis-trans* isomerization and to C-3 will give double-bond shift. The preponderance of *cis-trans* isomerization might be explained by steric hindrance at C-3. A steric effect can be considered to be less prominent at higher temperatures and a comparable phenomenon has been described before,<sup>23</sup> albeit under entirely different conditions, under which the intermediate was considered to be configurationally stable.

The reactions of the optically active limonene are in agreement with the suggested mechanism of consecutive hydrogen abstractions and additions. The most important observation, apparent from the data of Table IV, is the fact that conversion into the products of dehydrogenation, *p*-cymene and *p*-isopropenyltoluene, decreases much more than that of double-bond shift,

(21) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(22) M. H. Back and R. J. Cvetanovic, *Can. J. Chem.*, **41**, 1396 (1963).

(23) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

terpinolene and  $\alpha$ -terpinene. The fact that racemization of unconverted limonene, which we considered to be caused by a double-bond shift, decreases even more than the dehydrogenation cannot be explained without additional assumptions. It may be that either oxygen adsorbed on the surface is responsible or a different mechanism is active. Another reason might be that the double-bond shift, which causes inversion of configuration, demands the initial abstraction of a secondary allylic hydrogen, the isomerization into terpinolene, on the other hand, that of a tertiary one. The mechanism of racemization is being studied at the moment.

The inhibition of autoxidation as exhibited by pyrolyzed polyacrylonitrile, which is contrary to the behavior of several other semiconducting polymers,<sup>6</sup> could be sought in the polyaromatic quinoid structure, which has been sketched above. The same affinity which the polymer shows for atomic hydrogen might cause it to react with the reactive intermediates of the autoxidation chain.

The behavior of pyrolyzed polyacrylonitrile toward several compounds is thus in agreement with its proposed structure. An especially synthesized polymer, pyrolyzed polycyanoacetylene, which is thought to contain the same structural element, behaves in a similar way, and contrary to other carbonaceous materials. The study of the correlation between the chemical structure of polymers and their catalytic properties is being continued.

## Experimental

**Reagents.** Cyclohexene was made peroxide free by passing it over a column of acid-washed alumina (Merck reagent grade), and tested before each experiment with an acidified KI solution. (–)-Limonene (Fluka A.G., Switzerland) was shaken with a ferrous sulfate solution, distilled before use, and also tested for peroxide. Gas chromatographic analysis did not show any impurities in the cyclohexene; the limonene was 98% pure. The butenes were Mathieson C.P. and were used as supplied.

**Polymerization of Acrylonitrile.** Freshly distilled acrylonitrile (110 g.) was dissolved in 1500 ml. of water and the solution was kept at 60° under nitrogen while stirring vigorously. Azobisisobutyronitrile in two 1-g. portions, one at the start and one after 2 hr., was added. After an additional 2 hr., stirring and heating were stopped and the white polymer was sucked off and dried at 60° under vacuum to constant weight.

**Pyrolysis of Polyacrylonitrile.** The white, dry polymer was spread out in a thin layer, slowly heated to 230° in a draft oven, and kept at this temperature during 12 hr. During this period the color changed via yellow to brown.

**Preparation of Catalyst.** The brown powder, obtained after pyrolysis, was pelleted at 8000 p.s.i., crushed, and sieved between 12–25 mesh. The material thus obtained was heated in a nitrogen stream for 0.5 hr. at 450°. It turned from brown into black under these conditions.

**Anal.** Found: C, 56.08; H, 2.62; N, 16.59.

**Vapor Phase Reaction.** Reactions were run in a Pyrex tube which had been filled with a mixture of

catalyst and glass beads and was heated in a vertical oven. Liquid reagents were introduced in the upper tube by means of a syringe pump of variable speed. At the lower part of the tube, liquid products were condensed in a trap and gaseous products were collected in a gasometer over a saturated salt solution. The occurrence of thermal reactions was checked by runs in the same reactor in the absence of catalyst.

*Analysis.* Analyses were carried out by gas chromatography on an F & M 500 temperature-programmed gas chromatograph. The butenes were separated over a column 10 m. in length packed with dimethylformamide on Chromosorb at  $-20^{\circ}$ . The reaction products of cyclohexene were analyzed over Carbowax 20 M, programmed from 75 to  $200^{\circ}$  at  $11^{\circ}/\text{min}$ . The reaction products of 5-ethyl-5-methyl-1,3-cyclohexadiene were analyzed over  $\beta,\beta'$ -oxydipropionitrile at  $90^{\circ}$ . The products were identified by comparison with authentic samples.

*Autoxidation.* Cumene (400 ml., B.D.H., laboratory reagent) was shaken with 20-ml. portions of concentrated  $\text{H}_2\text{SO}_4$  until no color changes in the acid layer could be observed. After shaking with a 2 *N* NaOH solution and water, it was dried and distilled, b.p.  $152\text{--}154^{\circ}$ . Portions (10 ml.) of cumene were vigorously shaken at  $90^{\circ}$  under oxygen. Without the sulfuric acid treatment, no autoxidation took place.

*Synthesis of Cyanoacetylene.* Cyanoacetylene was synthesized<sup>24</sup> by dehydration of propargyl aldoxime by acetic anhydride. Propargyl aldehyde was obtained by oxidation of propargyl alcohol.<sup>25</sup>

*Polymerization of Cyanoacetylene.* Into a 100-ml., round-bottom flask containing a magnetic stirrer and 500 mg. of dry NaCN, 20 ml. of dimethylformamide (dried by azeotropic distillation with benzene) was distilled from molecular sieves under vacuum. After stirring to dissolve the NaCN as far as possible, the solution was cooled with liquid air and 2 ml. of cyanoacetylene was distilled in from  $\text{P}_2\text{O}_5$ , whereupon the solution immediately turned black. After stirring

(24) J. Happel, C. J. Marsel, and A. A. Reidlinger, U. S. Patent 3,006,948 (1962); *Chem. Abstr.*, **56**, 8574g (1962).

(25) *Org. Syn.*, **36**, 66 (1956).

at  $-50^{\circ}$  for 3 hr. and at room temperature for 12 hr., 0.25 ml. of water was added and the reaction mixture was poured into 750 ml. of dilute HCl to precipitate the polymer.

The black precipitate was solved in 20 ml. of dry acetone and filtered. The polymer was precipitated from the acetone solution by methylene chloride, filtered off, and dried over  $\text{P}_2\text{O}_5$ , yielding 1 g. (65%).

*Preparation of Polycyanoacetylene Catalyst.* The polymer was heated as such in a stream of dry nitrogen at  $450^{\circ}$  for 0.5 hr.; weight loss, most of which could be recovered as water, was 15%.

*Anal.* Calcd.: C, 70.59; H, 1.96; N, 27.45. Found: C, 69.96; H, 2.21; N, 27.21.<sup>26</sup>

Alternatively, boiling stones (Fisher "boileezers") were crushed, sieved, and heated in a  $\text{N}_2$  stream at  $450^{\circ}$  for 12 hr. Afterwards they were impregnated *in vacuo* with a solution of 300 mg. of polymer in 30 ml. of dry acetone. The acetone was evaporated *in vacuo* and the impregnated carrier heated for 0.5 hr. in a nitrogen stream at  $450^{\circ}$ .

*Surface area determination* was essentially according to the method of Nelsen and Eggertsen.<sup>28</sup> Samples were compared with two standards at a time.

*Synthesis of 5-Ethyl-5-methyl-1,3-cyclohexadiene.* The diene was synthesized as indicated by Pines and co-workers.<sup>16</sup>

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(26) Consistent results could only be obtained by outgassing the sample *in vacuo* at  $300^{\circ}$  for several hours, opening the ampoule immediately before weighing, and correcting for weight increase after opening (4.8 mg. of polymer increased  $50\ \mu\text{g.}/\text{min}$ ). Similar complications have been reported previously.<sup>27</sup>

(27) R. McNeill, R. Sjudak, J. H. Wardlaw, and D. E. Weiss, *Australian J. Chem.*, **16**, 1060 (1963).

(28) F. M. Nelsen and F. T. Eggertsen, *Anal. Chem.*, **30**, 1387 (1958).