p-Polyphenyl from Benzene–Lewis Acid Catalyst–Oxidant. Reaction Scope and Investigation of the Benzene–Aluminum Chloride–Cupric Chloride System[1]

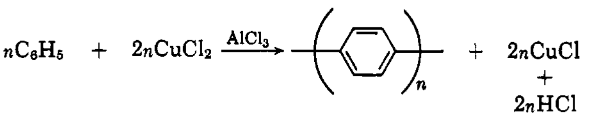
PETER KOVACIC AND JAMES OZIOMEK

The Department of Chemistry, Case Institute of Technology, Cleveland, Ohio

Received July 22, 1963

In the polymerization of benzene by aluminum chloride–cupric chloride, the yield of *p*-polyphenyl varied inversely with the amount of added water. Polymer yield attained a maximum value, almost quantitative, at an $AlCl_3$–$CuCl_2$ molar ratio of 2:1. The cuprous chloride formed by reduction of the oxidant is present as a $C_6H_6 \cdot AlCl_3 \cdot CuCl$ complex. Large amounts of added cuprous chloride inhibited the reaction completely, whereas smaller quantities acted as a promoter. With cupric halide as oxidant, aluminum chloride, aluminum bromide, and antimony pentachloride exhibited catalytic activity. In the presence of aluminum halide catalyst, polymerization occurred with the oxidizing agents, cupric chloride, cupric bromide, lead dioxide, manganese dioxide, nitrogen dioxide, nitrogen trioxide, chloranil, and *p*-benzoquinone. There was evidence of chain termination by the nitrogen oxides and chloranil. The theoretical aspects are treated.

Recently, it was shown[2] that the aromatic nucleus can be polymerized smoothly in the system, aromatic monomer–Lewis acid catalyst–oxidant. This constituted the first case wherein an aromatic monomer functioned in a well defined polymerization leading to homopolymer. For example, benzene was converted to *p*-polyphenyl on treatment with aluminum chloride–cupric chloride under mild conditions.



Also effective for the polymerization of benzene were molybdenum pentachloride[3] and ferric chloride.[4] These two metal halides apparently assume the dual role of catalyst and oxidant. Prior to these investigations Marvel and Hartzell[5] synthesized impure *p*-polyphenyl by the chloranil oxidation of poly-1,3-cyclohexadiene prepared by Ziegler polymerization.

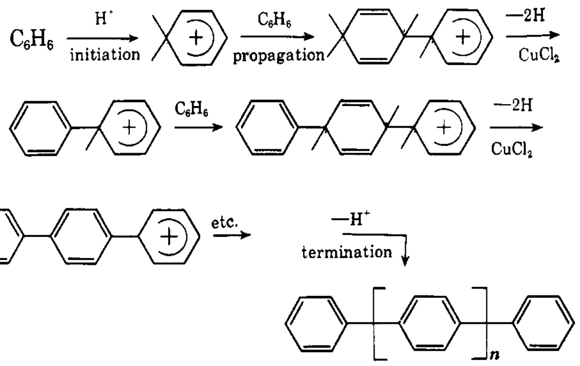
The purpose of this study was to define the scope of benzene polymerization in the system, benzene–Lewis acid catalyst–oxidant. In particular, the reaction benzene–aluminum chloride–cupric chloride was explored, in order to determine the effect of water, cuprous chloride, and variation in catalyst–oxidant ratio. In addition, we were interested in obtaining information relative to the mechanistic aspects of this novel reaction.

Results and Discussion

Water Cocatalysis.—Previously, evidence was found in the benzene–ferric chloride reaction for cocatalysis by Brønsted acids, such as water, acetic acid, and nitroethane.[6] Subsequently, it was shown that the polymer yield passed through a maximum at a H_2O–$FeCl_3$ molar ratio of 1 for short reaction times. Furthermore, the most rapid rate of hydrogen chloride evolution was observed at this ratio.[7] These data indicate that ferric chloride monohydrate is the most active catalyst–cocatalyst complex.

In view of these results, we undertook an investigation of water as a potential cocatalyst in the benzene–aluminum chloride–cupric chloride reaction. The following working hypothesis was used.

$$H_2O + AlCl_3 \rightleftarrows H_2O \cdots AlCl_3 \rightleftarrows H^+AlCl_3(OH)^-$$



Water was added to the system, C_6H_6–$AlCl_3$–$CuCl_2$ = 4:1:1 (2 hr. at 30–32°), in molar ratios of H_2O–$AlCl_3$ varying from 0 to 4. The results clearly show that polymer yield varies inversely with the amount of added water (Table I). This is in sharp contrast with

TABLE I

VARIATION OF WATER. EFFECT ON POLYMER YIELD[a,b]

	p-Polyphenyl					
H_2O, moles	Yield, %	%				C-H, atomic ratio
		C	H	Cl	O	
0	64	92.29	5.03	2.47		1.53
0	66	91.79	5.07	2.29		1.50
0.05	60	93.43	5.05	1.62		1.54
0.05	56	92.21	5.00	2.40		1.54
0.25	29	91.48	5.04	2.43	0.49	1.51
0.25	30	92.66	5.07	1.79	0.22	1.52
0.5	17	93.32	5.38	1.38	0.31	1.44
0.5	18	92.25	5.05	1.42		1.52
1	8[c]	92.72	5.21	1.87		1.48
1	17	92.51	5.30	2.13	0.30	1.45
1	13	92.56	5.15	2.17	0.32	1.49
1.5	0.8[d]	84.00	4.74	1.95	1.37	1.47
1.5	3	91.17	5.37	2.01	0.46	1.41
2	0.13[e,f]	57.46	3.31	4.96	10.80	1.44
2	0.1[f]	26.45	2.57	3.07	2.75	0.83

[a] Benzene, 2 moles; aluminum chloride, 0.5 mole; cupric chloride, 0.5 mole. [b] 2 hr. at 30–32°. [c] 17°. [d] 25°. [e] 81°. [f] Probably contains a high per cent of contaminants from impurities in the metal halides.

---

(1) Paper VI, Polymerization of Aromatic Nuclei [undergraduate thesis of J. Oziomek, Case Institute of Technology, 1963] presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

(3) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

(4) P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963).

(5) C. S. Marvel and G. E. Hartzell, *J. Am. Chem. Soc.*, **81**, 448 (1959).

(6) P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960).

(7) P. Kovacic, F. W. Koch, and C. E. Stephan, *ibid.*, in press.

the data already cited for ferric chloride. A plausible interpretation involves the destruction of aluminum chloride by hydrolysis, on the assumption that large amounts of catalyst are required for high yields. It is evident that hydrolysis does occur at an appreciable rate under the standard conditions. When 0.25 mole of water was added, analysis indicated the evolution of 0.38 mole of hydrogen chloride, corresponding to a polymer yield of 14.4 g. However, only 5.7 g. of polymer was formed, which is equivalent to only 0.15 mole of hydrogen chloride. Consequently, hydrolysis must account for the remaining 0.23 mole of hydrogen chloride. Moreover, hydrogen chloride was generated when water was stirred with a cold mixture of benzene and aluminum chloride.

It is conceivable that some water is consumed in a chain termination reaction, which is in keeping with the presence of small amounts of oxygen in the polymers. However, there was no simple correlation which was apparent entailing oxygen content and the amount of added water.

Although no evidence was obtained for water cocatalysis, it is quite possible that small amounts of this or some other Brønsted acid are necessary for initiation. We have not yet investigated the reaction with rigorously purified reagents. The need of a Brønsted acid cocatalyst has been unequivocally establishd for many olefin polymerizations induced by Lewis acids.[8,9] In certain cases, only trace amounts of cocatalyst are needed. Furthermore, various studies point to an optimum quantity, with diminution in the activity of the catalyst–cocatalyst complex with added amounts of cocatalyst, presumably due to formation of more highly solvated entities.[8,10]

There are other reports which lend credence to these postulates. The rate curve for isobutylene polymerization leveled out at approximately equimolar proportions of catalyst and cocatalyst, as the amount of stannic chloride was increased at a fixed water concentration.[10] The effect on rate of varying the water concentration in the polymerization of styrene catalyzed by stannic chloride was determined by Overberger, Ehrig, and Marcus.[11] In a 30:70% mixture of nitrobenzene and carbon tetrachloride, the rate increased as the water concentration increased, reached a maximum at a 1:1 catalyst–cocatalyst molar ratio, and then decreased upon further addition of water. The system styrene-boron trifluoride–water is reported to give similar results.[8,9]

Variation in $AlCl_3$–$CuCl_2$.—In another series of experiments, the effect of variation in the $AlCl_3$–$CuCl_2$ molar ratio was investigated at temperatures of 30–32° for 2 hr. The yield of polymer rose rapidly with increasing molar ratio, reached a maximum at a 2:1 ratio and then remained essentially constant (Table II). It is noteworthy that yields approaching quantitative values were readily and reproducibly obtained. At the optimum ratio and with pulverized cupric chloride, the rapid polymerization produced *p*-polyphenyl in 98% yield based on the oxidant.

TABLE II

VARIATION OF $AlCl_3$–$CuCl_2$ RATIO: EFFECT ON POLYMER YIELD[a]

$AlCl_3$–$CuCl_2$, molar ratio	*p*-Polyphenyl Yield, %	% C	H	Cl	C–H, atomic ratio
0.125:0.5	18	90.69	5.03	1.80	1.50
0.25:0.5	35	91.36	4.95	2.33	1.53
0.25:0.5[b]	34	89.04	4.74	4.02	1.56
0.5:0.5	64	92.29	5.03	2.47	1.53
0.5:0.5	66	91.79	5.07	2.29	1.50
1.5:1.5[c,d]	65	92.90	5.22	2.15	1.48
1.5:1.5[c,d]	63	92.31	5.10	2.25	1.51
0.5:0.25[e]	89	92.09	4.79	2.37	1.60
0.5:0.25	94	90.06	5.06	3.29	1.48
0.5:0.25[f]	91	91.15	5.00	1.75	1.52
0.5:0.25[g]	98	91.37	5.12	1.71	1.48
1.5:0.75[d]	91	92.40	5.28	2.71	1.46
1.5:0.75[d]	89[h]	91.75	5.10	1.73	1.50
1.5:0.75[d,i]	91	91.24	5.12	2.39	1.48
0.5:0.125	89	91.30	5.03	2.54	1.51

[a] Benzene, 2 moles; 2 hr.; 30–32°; no added water. [b] The aluminum chloride was pulverized in a blender with benzene. [c] By Richard Lewis, 30–36°; the cupric chloride was pulverized in a blender with benzene. [d] Benzene, 6 moles. [e] 1.5 hr. [f] 27.5 hr. [g] Pulverized cupric chloride. [h] 87% yield of hydrogen chloride. [i] By Vincent Marchionna.

Why the necessity for large quantities of the catalyst? In response to this question, we determined the influence of initially added cuprous chloride. Very strikingly, essentially no polymerization occurred, even at the reflux temperature, when cuprous chloride and aluminum chloride were used in an equimolar ratio.

At a CuCl-$AlCl_3$ molar ratio of 1:2, the yield (39%) corresponded closely to that (35%) obtained with half this amount of aluminum chloride in the absence of added cuprous chloride. These findings strongly support the thesis that cuprous chloride, generated during the course of the C_6H_6–$AlCl_3$–$CuCl_2$ reaction, acts as a powerful inhibitor by associating with aluminum chloride. The union apparently results in a 1:1 complex which contains the aluminum chloride in catalytically inactive form.

In further pursuit of this intriguing phenomenon, the benzene filtrate obtained from one of the reaction mixtures was examined. Addition of water to the dark green solution produced an exothermic reaction resulting in evolution of acid fumes and precipitation of copious amounts of cuprous chloride. Since the salt itself is very insoluble in benzene, this observation compellingly argues for the presence of cuprous chloride in complex form. Confirmation was readily obtained from solubility experiments (Table III). Although cuprous chloride and aluminum chloride individually were only slightly soluble (<3%) in benzene, a mixture containing equimolar amounts of the two salts dissolved almost completely at room temperature with formation of a yellow solution.

TABLE III

SOLUBILITY OF METAL HALIDES IN BENZENE[a]

$AlCl_3$ g.	Mole	CuCl g.	Mole	Solid, g. Undissolved	Dissolved
16.66	0.125	0		16.00	0.42
0		12.40	0.125	12.25	0
16.70	0.125	12.40	0.125	1.4	27.1

[a] Benzene, 0.5 mole.

---

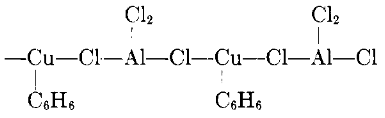
(8) "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., W. Heffer and Sons, Ltd., Cambridge, England, 1953.

(9) D. C. Pepper, *Quart Rev.* (London), **8**, 88 (1954).

(10) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, **48**, 91 (1952).

(11) C. G. Overberger, R. J. Ehrig, and R. A. Marcus, *J. Am. Chem. Soc.*, **80**, 2456 (1958).

When our studies were essentially complete, Amma and Turner[12] presented their work on this hitherto unreported complex. A detailed X-ray analysis revealed that the compound was formed in the ratio, C_6H_6–CuCl–$AlCl_3$ = 1:1:1, and possessed this structure.


$$\begin{array}{c}\quad Cl_2 \qquad\qquad Cl_2 \\ -Cu-Cl-Al-Cl-Cu-Cl-Al-Cl \\ C_6H_6 \qquad\qquad C_6H_6\end{array}$$

Cuprous bromide is known[13] to form similar complexes, such as $C_6H_5CH_3{\cdot}CuBr{\cdot}AlBr_3$. In related areas, Brown and Wallace[14] found evidence for the existence of arenonium-type entities, $ArH_2{}^+Al_2X_7{}^-$, which were solvated by the aromatic substrate. Quite thorough structural analyses have been made of the benzene–silver perchlorate complex.[15]

The reactions carried out at 30–32° in the absence of added water are characterized by induction periods varying from 15 to 25 min. Much to our surprise, we observed that cuprous chloride virtually eliminated the induction period when introduced in the ratio, CuCl–$AlCl_3$ = 1:2. Thus the cuprous chloride may function both as an inhibitor and a promoter. Although the precise nature of the promoting action is unknown, there are several conjectures deemed worthy of consideration. The cuprous chloride might be an efficient catalyst at some stage in the reaction sequence. Another possibility is that a cuprous–cupric complex[16] comprises the actual dehydrogenating agent. However, in one of the solubility experiments cupric chloride proved to be quite insoluble in benzene containing the $C_6H_6{\cdot}CuCl{\cdot}AlCl_3$ complex. It is significant that cuprous bromide exerts a similar accelerating effect in the bromination of toluene by cupric bromide.[17]

Essentially identical infrared spectra were exhibited by preparations of *p*-polyphenyl obtained under the various conditions. The C–H atomic ratios fell in the range, 1.41–1.60, with an average value of 1.50. These data compare favorably with the limiting ratio of 1.5 for $(-C_6H_4-)_n$.

Gas chromatographic analysis of the benzene filtrate from the reaction mixture revealed the presence of biphenyl and chlorobenzene in small quantities. Presumably, biphenyl derives from termination at the dimer stage of polymerization. Chloro aromatics might be formed through termination of the growing carbonium ion by chloride, or by chlorination effected by cupric chloride–aluminum chloride.[18]

One aspect of the mechanistic scheme[2] comprises transformation of dihydrobenzene structures to aromatic units. Previously, in investigations with the model compound, 1,4-cyclohexadiene, it was shown that benzene was readily formed on treatment with ferric chloride[4] or molybdenum pentachloride.[3] Analogous experiments were carried out with the metal halides present in our system (Table IV). Neither cupric chloride nor cuprous chloride produced detectable reaction with 1,4-cyclohexadiene. With aluminum chloride or aluminum chloride–cupric chloride, polymerization of the diene was the preferred route. However, using toluene as solvent, we found that benzene was formed with the reagents, aluminum chloride–cupric chloride–cuprous chloride and aluminum chloride–cuprous chloride. These data intimate that the Lewis acid catalyst participates in dehydrogenation by the oxidant. A more detailed discussion should be deferred until these preliminary results are expanded by additional studies. It is significant that 9,10-dihydroanthracene is smoothly dehydrogenated by cupric halides under mild conditions.[19]

TABLE IV

DEHYDROGENATION OF 1,4-CYCLOHEXADIENE[a]

Mole			Temp., °C.	Time, min.	Results
$AlCl_3$	CuCl	$CuCl_2$			
0.01	0	0	10	~1	Polymerization
0	0.01	0	40	5	No reaction
0	0	0.01	40	5	No reaction
0.01	0	0.01	10	~1	Polymerization
0.01	0.011[b]	0	40	5	Benzene formed
0.01	0.011[b]	0.01[c]	40	5	Benzene formed[d]

[a] 1,4-Cyclohexadiene (1 ml.) in 15 ml. of toluene. [b] The toluene–aluminum chloride–cuprous chloride complex was formed before the addition of 1,4-cyclohexadiene. [c] Cupric chloride was added to the $C_7H_8{\cdot}CuCl{\cdot}AlCl_3$ complex before the 1,4-cyclohexadiene. [d] Hydrogen chloride was evolved.

Although we favor the oxidative cationic mechanism for the polymerization, alternative possibilities should also be considered. For example, the high degree of selectivity for 1,4-polymerization suggests that perhaps a surface effect involving metal halide plays an important role.

Benzene–Lewis Acid Catalyst–Oxidant.—A large number of candidate catalysts and oxidants were examined in an effort to ascertain the reaction scope. With cupric halide as the oxidant, polymerization to *p*-polyphenyl was accomplished only by those metal halides which possess rather high Lewis acid strength, namely, aluminum chloride, aluminum bromide, and antimony pentachloride (Table V). Ferric chloride[4] and molybdenum pentachloride[3] were previously shown to be active. It is interesting that antimony pentachloride alone, or in conjunction with aluminum chloride, gave only chlorinated benzenes.[20] A direct correlation apparently exists between ease of monomer polymerization and catalyst strength requirement. In contrast to the benzene reaction, cationic polymerization of olefins proceeds under very mild conditions, at −100° within a few seconds in the presence of a relatively weak catalyst such as boron trifluoride.

Specificity was evident relative to the nature of the oxidant. With aluminum halide as catalyst, polymer was generated by use of the following oxidizing agents: cupric chloride, cupric bromide, lead dioxide, manganese dioxide, nitrogen trioxide, nitrogen dioxide, chloranil, and *p*-benzoquinone (Table V).

Infrared spectral data (Table VI) and elemental analyses of the polymers were in agreement with a *p*-

---

(12) E. L. Amma and R. Turner, Abstracts of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 12K.

(13) V. A. Plotnikov and Z. A. Yankelevich, *J. Gen. Chem. USSR*, **3**, 208 (1933); V. A. Plotnikov, Z. A. Yankelevich, and I. A. Sheka, *ibid.*, **3**, 802 (1933).

(14) H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6268 (1953).

(15) H. G. Smith and R. E. Rundle, *ibid.*, **80**, 5075 (1958).

(16) J. K. Kochi, *ibid.*, **77**, 5274 (1955); H. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

(17) K. Davis, unpublished work.

(18) J. C. Ware and E. E. Borchert, *J. Org. Chem.*, **26**, 2263, 2267 (1961).

(19) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).

(20) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960).

TABLE V

POLYMER FROM BENZENE–CATALYST–OXIDANT[a]

				Polymer						
					%					
Catalyst	Oxidant	Time, hr.	Temp., °C.	Yield, g.	C	H	Halogen	N	O	C-(H + halogen), atomic ratio
$AlBr_3$	$CuBr_2$[b]	4.3	25	1.8[c]	87.77	5.17	6.81			1.39
$AlCl_3$	MnO_2	6	80	7.8[d,e,f]	67.71	3.65	21.10		4.10	1.33
$AlCl_3$	PbO_2	1	80	9.4[d,e,g]	79.58	4.22	14.07		2.00	1.44
$AlCl_3$	Chloranil	1	Reflux	8.3[c,h]	76.41	3.34	11.31		5.15	
$AlCl_3$	*p*-Benzoquinone	2	Reflux	1.7[h]	73.15	3.07	4.98		13.3	
$AlCl_3$	NO_2[i]	1	Reflux	2.5	85.07	4.40	4.55	0.87		1.56
$AlCl_3$	N_2O_3[i]	1	Reflux	1.2	85.09	4.41	4.15	0.84		1.57
$SbCl_5$	$CuCl_2$	4	5	1.9[j]	90.40	5.10	3.43			1.45

[a] Benzene, 2 moles; catalyst, 0.5 mole; oxidant, 0.5 mole. [b] Water cocatalyst, 0.025 mole; the assistance of F. J. Kohl is gratefully acknowledged. [c] Run at half-scale. [d] By A. Kyriakis. [e] Benzene, 1 mole; water, 1 ml. [f] *d*-Spacings: 4.22 and 9.30 Å., from X-ray powder pattern. [g] *d*-Spacings; 2.67, 4.35, and 7.75 Å., from X-ray powder pattern. [h] After exhaustive extraction with boiling ethanol. [i] The gas (undetermined amount) was introduced below the surface of the mixture. [j] Also C_6H_5Cl, $C_6H_4Cl_2$, and $C_6H_3Cl_3$.

TABLE VI

INFRARED SPECTRAL DATA FOR THE POLYMERS

	Absorption maxima, cm.$^{-1}$			Peak height ratios,
p-Polyphenyl	*para*	mono		*para*-(mono$_1$ + mono$_2$)
p-Terphenyl[a]	837	746	687	1:(1.12 + 1.0) = 0.47
p-Quaterphenyl[a]	825	752	687	1:(1.04 + 0.87) = 0.52
p-Quinquephenyl[a]	818	757	688	1:(1.0 + 0.79) = 0.56
p-Sexiphenyl[b]	811	756	682	1:(1.06 + 0.41) = 0.68
C_6H_6–$AlCl_3$–N_2O_3[c]	807	760	696	1:(0.83 + 0.75) = 0.63
C_6H_6–$AlCl_3$–NO_2[c]	806	762	697	1:(0.62 + 0.49) = 0.90
C_6H_6–$AlCl_3$–chloranil[d]	805	765	695	1:(0.51 + 0.25) = 1.32
C_6H_6–$AlCl_3$–$CuCl_2$	803	763	693	1:(0.18 + 0.04) = 4.55
C_6H_6–$AlBr_3$–$CuBr_2$	803	760	690	1:(0.14 + 0.02) = 6.25
C_6H_6–$SbCl_5$–$CuCl_2$	802	758	690	1:(0.09 + 0.03) = 8.35

[a] Data from A. Kyriakis. [b] Data from R. M. Lange. [c] Additional band at 1592 cm.$^{-1}$. [d] Additional minor bands at 740, 1425, 1324, 1213, and 933 cm.$^{-1}$.

polyphenyl structure, with the possible exception of the products derived from *p*-benzoquinone and chloranil. The dark polymer obtained from *p*-benzoquinone gave an ill-defined spectrum which, nevertheless, was suggestive of *p*-polyphenyl. In the case of chloranil, the product spectrum exhibited many absorption bands in addition to those characteristic of *p*-polyphenyl. It is conceivable that copolymers are formed from the benzene–quinone–aluminum chloride reactions. Nitrogen dioxide and nitrogen trioxide yielded polymers which were very similar to each other.

Examination of the infrared spectral data leads to the conclusion that the polymers prepared with the nitrogen oxides and chloranil possess lower molecular weights than the others. An approximate indication of relative molecular weights in the *p*-polyphenyl series may be obtained from the ratio, intensity (*para* band)–intensity (mono bands). The characteristic absorption maxima fall in the regions, 802–807 (*para*), 758–765 (mono), and 690–697 cm.$^{-1}$ (mono). As the molecular weight increases, this ratio becomes larger. The values for the polymers obtained with $AlCl_3$–$CuCl_2$, $AlBr_3$–$CuBr_2$, and $SbCl_5$–$CuCl_2$ lie in the range 4.5–8.4, as compared with 0.6–1.3 for the products from $AlCl_3$–NO_2, $AlCl_3$–N_2O_3, and $AlCl_3$–chloranil.

The inference can be drawn that the nitrogen oxides and chloranil also function as chain terminators. Brown and Mathieson[21] found that *p*-benzoquinone retarded or completely inhibited the cationic polymerization of styrene. Furthermore, the molecular weight of the polystyrene was decreased in proportion to the quinone concentration, which suggests interaction of quinone with the propagating carbonium ion. The 0.87% nitrogen in the *p*-polyphenyls generated with nitrogen oxides is most likely incorporated in nitro groups. On the assumption that one such group is present per molecule through chain termination, an average chain length of *ca.* eighteen benzene rings would apply. The position of the mono bands in the infrared spectrum points to a *p*-polyphenyl containing a *para* substituent. It may be that some nitro groups are situated along the backbone of the chain.

Since water is most likely generated in the nitrogen oxide systems, it is reasonable to consider a nitrogen-containing Brønsted acid as a possible terminator, in addition to the free nitrogen oxides. Of pertinence in this connection is the conversion of an alkyl halide to nitroalkane and nitrite ester by reaction with a nitrite salt.[22] By analogy, termination also could occur with formation of nitrite ester end groups which subsequently would be subjected to hydrolytic conditions. The literature contains evidence for retardation and inhibition of cationic polymerization by nitro bodies, such as nitrobenzene.[8,21]

Titov, who previously examined the benzene–nitrogen dioxide–aluminum chloride reaction under somewhat different conditions, was concerned primarily with aromatic nitration.[23] Good yields of simple nitrated products were reported from benzene, toluene, and chlorobenzene, with nitrosyl chloride[24] as a by-

---

(21) C. P. Brown and A. R. Mathieson, *J. Chem. Soc.*, 3612 (1957).

(22) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961 p. 128.

(23) A. I. Titov, *J. Gen. Chem. USSR*, **7**, 591 (1937).

(24) J. D. Archambault, H. H. Sisler, and G. E. Ryschkewitsch; *J. Inorg. Nucl. Chem.*, **17**, 130 (1961).

product. Nitration of aromatic nuclei also has been accomplished with boron trifluoride complexes[25] of dinitrogen tetroxide and nitrogen trioxide. In general, we did not investigate the low molecular weight fraction of the reaction mixtures.

Whereas the polyphenyl from cupric chloride contained only small amounts of chlorine (about 2%), halogenation was much more extensive (14–21%) with manganese dioxide and lead dioxide. Since these oxides readily oxidize hydrogen chloride,[26] subsequent catalytic chlorination of the *p*-polyphenyl most likely involves the generated chlorine. Hydrolysis of aluminum chloride, by water formed during polymerization, would serve as a plausible source of hydrogen chloride. The corresponding metal tetrahalides[27] might also arise *in situ* as reactive intermediates. In the case of the polymers (4% chlorine) synthesized with nitrogen oxides, nitrosyl chloride may be the halogenating species in view of its ability to chlorinate the aromatic nucleus.[28]

Experimental[29]

Benzene–Aluminum Chloride–Cupric Chloride. General Procedure.—A mixture of dry, thiophene-free benzene (2 moles) and anhydrous aluminum chloride (0.5 mole) was covered with an atmosphere of dry nitrogen. When water was used, addition was made dropwise to the stirred mixture at 6–10°. Then anhydrous cupric chloride (0.5 mole, dried at 120°) was added, and the mixture was heated to 30–32°. After an induction period of about 25 min., the contents assumed a purple-black color, and acid gas was evolved, which, in most cases, was followed by titration with standard caustic.

The reaction was allowed to proceed with efficient stirring for 2 hr. from the time of initiation. The mixture was then cooled to 15° and was either (1) added to 1.4 l. of ice-cold 18% hydrochloric acid, or (2) filtered, followed by addition of the residue to acid solution. The mixture of crude polymer and aqueous acid was heated at the boil, filtered, and the residue washed with water. After the solid was pulverized briefly in a blender with water, it was triturated with boiling 18% hydrochloric acid until the filtrate was colorless. Washing with boiling distilled water was continued until the test (silver nitrate) for chloride ion was negative. The product, dried at 120°, was a finely divided, light brown solid. Care was taken to avoid contamination.

A similar procedure was used with other catalyst–oxidant systems.

Average values for duplicate analyses are recorded in the tables. Maximum deviations were C, ± 0.2; H, ±0.15; Cl, ±0.2. Occasionally, an erratic analysis was obtained which was discarded after appropriate checking. Polymer yields (%) are based on cupric chloride.

Reaction Products. A. Cuprous Chloride.—The reaction mixture from benzene (2 moles)–aluminum chloride (0.5 mole)–cupric chloride (0.5 mole), 2 hr. at 31–32°, was filtered directly. Water was slowly added with stirring to the dark green filtrate until no further reaction occurred. After filtration, the white solid was washed under nitrogen with dilute hydrochloric acid and then with water. Drying was accomplished *in vacuo* at 100° to yield 21.8 g.

Anal. Calcd. for CuCl: Cu, 64.2. Found: Cu, 63.39.

The X-ray diffraction pattern[30] gave the *d*-spacings, Å.: 3.10, 1.90, 1.625, 0.891, and 0.861. Authentic cuprous chloride gave identical *d*-spacings. Essentially the same pattern is reported[31] for cuprous chloride.

B. Organic By-products.—The benzene solution from part A was separated from the aqueous portion, washed first with dilute acid and then with water, and dried over sodium sulfate. After distillation of the benzene through a helices-packed column, the residue was subjected to gas chromatography. Characterization was accomplished by retention times, infrared spectrum (for chlorobenzene product, identical with that of authentic material), and the ultraviolet spectrum (for biphenyl, λ_{max} 248 mμ, lit.[32] λ_{max} 248 mμ).

Benzene–Aluminum Chloride–Cupric Chloride–Cuprous Chloride. A.—After the addition of cupric chloride (0.25 mole) to a mixture of benzene (1 mole), aluminum chloride (0.25 mole) and cuprous chloride (0.25 mole) under nitrogen, stirring was maintained for 1 hr. at 31–32° and for 1 hr. at reflux. Work-up yielded only a trace of polymer.

B.—Cupric chloride (0.25 mole) was added to a mixture of benzene (1 mole), aluminum chloride (0.25 mole), and cuprous chloride (0.125 mole) at 25° with stirring under nitrogen. The reaction mixture immediately became dark and hydrogen chloride was evolved in a few seconds. After 2 hr. at 31–32°, the polymer was isolated by the usual procedure, 2.4 g. (39%).

Anal. Found: C, 90.72; H, 4.84; Cl, 3.37. Therefore, C–H = 1.56.

Solubility of Metal Halides in Benzene. A.—A mixture of the metal halide [aluminum chloride (0.125 mole), cuprous chloride (0.125 mole), or aluminum chloride (0.125 mole)–cuprous chloride (0.125 mole)] and benzene (0.5 mole) was stirred at reflux under nitrogen for 30 min. The mixture was allowed to cool to 25° and filtered. The amounts of undissolved and dissolved material were determined by vacuum drying of the solid at 80°, and by evaporation of the benzene filtrate *in vacuo* followed by drying of the residue. The results are summarized in Table III.

B.—A solution of the $C_6H_6 \cdot CuCl \cdot AlCl_3$ complex was formed from benzene (1 mole), cuprous chloride (0.137 mole), and aluminum chloride (0.125 mole) by vigorous shaking for 5 min. After filtration from a small amount of undissolved solid, cupric chloride (8.40 g., 0.0625 mole) was added to the clear light-yellow filtrate. The mixture was shaken well, filtered, and the solid washed with benzene. The recovered material, which was dried at 110°, weighed 8.35 g.

Dehydrogenation of 1,4-Cyclohexadiene.—To a cooled mixture of toluene and the appropriate metal halides was added 1 ml. of 1,4-cyclohexadiene. If no noticeable reaction occurred, the mixture was warmed in a water bath at 40° for 5 min. with stirring. For those systems containing metal halides in solution, dilute hydrochloric acid was added to destroy the complex before gas chromatography. The other reaction mixtures were chromatographed directly after the metal salts had settled out.

In a control experiment with toluene and aluminum chloride, there was no evidence for the formation of benzene.

Benzene–Catalyst–Oxidant. No *p*-Polyphenyl.—Essentially no polymer was obtained from benzene–aluminum chloride at the reflux temperature with the following candidate oxidants ($AlCl_3$–oxidant ratio was usually 1): cuprous chloride, mercuric chloride, mercurous chloride, phosphorus pentachloride, nitrobenzene, nitromethane, sulfur, nitric oxide, antimony pentachloride, barium peroxide, and air.

The following catalyst–oxidant combinations (usually 1:1 molar ratio) failed to produce polymer with benzene at reflux: zinc chloride, titanium tetrachloride, stannic chloride, sulfuric acid, or boron trifluoride with cupric chloride; sulfuric acid, hydrogen chloride, phosphoric acid, or phosphorus pentoxide with manganese dioxide; hydrogen chloride–lead dioxide.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The contributions of Mr. Alexander Kyriakis are gratefully acknowledged.

---

[25] G. B. Bachman, H. Feuer, B. R. Bluestein, and C. M. Vogt, *J. Am. Chem. Soc.*, **77**, 6188 (1955); G. B. Bachman and T. Hokama, *ibid.*, **79**, 4370 (1957).

[26] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, Oxford, England, 1952, p. 600; Vol. II, p. 1272.

[27] H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., Englewood Cliffs, N. J., p. 83.

[28] L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951).

[29] Elemental analyses were done by Dr. Weiler and Dr. Strauss, Oxford, England, and by Geller Laboratories, Bardonia, N. Y. The infrared spectra were obtained by the potassium bromide pellet technique.

[30] We are grateful to R. M. Lange for the X-ray data.

[31] H. E. Swanson, R. K. Fuyat, and G. M. Ugrinic, "Standard X-Ray Diffraction Powder Patterns," National Bureau of Standards Circular 539, Vol. IV, p. 35.

[32] E. H. Smith, Polyphenyls: Literature Search, U. S. Atomic Energy Commision, ER-8098, 1956.