[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Polymerization Induced by Hydrogen in Metals*

BY GIUSEPPE PARRAVANO

Hydrogen adsorbed on metals is generally assumed to be present in the atomic form. Similarly, it is generally agreed that, during the electrolysis of water, hydrogen atoms are formed, as intermediate species, at cathodic surfaces. In the present work, hydrogen liberated during processes of electrolysis or adsorbed at metal surfaces has been shown to cause initiation of polymerization in solutions of methyl methacrylate (MMA). A similar result for electrolytic systems has already been briefly reported by Wilson[1] with vinyl monomers.

The production of "free" hydrogen atoms at cathodic surfaces was claimed by Kobosew and Nekrassow,[2] who used as an indicator of hydrogen atoms the color changes involved in the reduction of a WO_3–water suspension. Prior to this research, Bodenstein,[3] studying the diffusion of hydrogen through a metal cathode could not obtain clean-cut evidence for the presence of hydrogen atoms in the gas which had left the cathode.

Experimental

Induction of polymerization during electrolysis was studied in a U-shaped cell with anodic and cathodic compartments separated by a sintered glass disk. The composition of the electrolyte was 0.1 *N* H_2SO_4 which was also 0.106 *M* in MMA. The latter was purified as previously described.[4] Cathodes of Pd, Pt, Zn, Pb, Cu and Ni in the form of foils were prepared from commercial metals.

Hydrogen adsorbed on metals was secured in a variety of ways. "Copper hydride" was prepared, according to Vanino,[5] by the action of sodium hypophosphite on a dilute solution of cupric sulfate at 70°. The red-brown precipitate was filtered and washed thoroughly with distilled water.

Titanium hydride was a commercial product.

Palladium, loaded with hydrogen, was obtained from a vacuum-fused and annealed foil, 0.001 in. thick, and made cathode in an electrolytic cell. With 0.1 *N* H_2SO_4 as electrolyte and a smooth platinum anode, electrolysis proceeded for 3 hours at a current density of 8.4 ma./sq. cm.

Palladium and nickel loaded with hydrogen were also obtained in a special cell as shown in Fig. 1. The electrolytic solution (0.1 *N* H_2SO_4) was contained in A. In B there was an aqueous solution of MMA. The solutions were separated by the cathode foil, 0.001 in. thick. The anode was platinum. Hydrogen liberated in the electrolysis diffuses through the cathode and initiates polymerization in B.

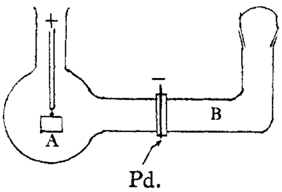

Fig. 1.

Electrolytic iron was prepared by electrolysis of a solution of 340 g./l. $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$, 2.5 g./l. H_2SO_4, c.d. = 40 ma./sq. cm. at 70°. Iron electrodes were used.

Electrolytic Cr was obtained by electrodeposition from a solution containing 250 g./l. CrO_3, 2.5 g./l. H_2SO_4, c.d. = 200 ma./sq. cm. at 60°, cathode Cu, anode Pb.

Electrolytic Co was prepared by electrodeposition on a copper cathode from a solution of $CoCl_2 \cdot 6H_2O$ 200 g./l., H_3BO_3 30 g./l., c.d. = 40 ma./cm.^{2} at 25°; anode, smooth Pt.

Chemisorbed hydrogen on ruthenium and nickel commercial powders and on platinum and palladium blacks was obtained in the following way: a series of test-tubes were filled with a definite amount of monomer–water solution and metal powder. After careful degassing by repeated freezing and evacuation, hydrogen at one atm. was introduced into the system, which was then kept at constant temperature. The time necessary for the formation of a white turbidity in the clear solution and for the precipitation of the polymer product was taken as an indication of the relative speed of the polymerization reaction.

Chemisorbed hydrogen on Ni was also obtained by reduction of NiO in a stream of hydrogen at 280° for 10 hours. Hydrogen was purified over Cu at 400°, palladium–asbestos at 200° and dried over solid $CaCl_2$ and in a trap cooled to −195°. After reduction, the sample was cooled slowly to room temperature in a stream of hydrogen. The aqueous solution of MMA was added to it, with the aid of an apparatus devised to exclude air.

Results

Results obtained for the electrolytic systems are recorded in Table I. All solutions used were deaerated with oxygen-free nitrogen.

TABLE I

CATHODIC POLYMERIZATION OF MMA SOLUTIONS AT 24°. C.D. FOR SOLID METALS = 2.57 MA./SQ. CM.

Cathode	Anode	Polymer formed, hr.	Hydrogen overvoltage[a]
Pt	Pt	>24	0.07
Pd	Pt	>24	
Ni	Pt	~18	.74
Cu	Pt	~10	.58
Zn	Pt	~ 6	.75
Pb	Pb	2	1.09
Hg	Pt	1.5	

[a] In 1 *M* H_2SO_4 solution, c.d. 10^{-2} amp./cm.^{2} from Latimer. "The Oxidation States of the Elements," Prentice-Hall, Inc., New York, N.Y., 1938, p. 29.

These data point to a close relationship between the efficiency of a particular metal to give rise to cathodic polymerization and its hydrogen overvoltage.

In Table II results are recorded for metals loaded cathodically with hydrogen.

TABLE II

INTERACTION OF METALS LOADED WITH HYDROGEN AND MMA AQUEOUS SOLUTION AT 24°

Sample	Time of cathodic treatment, hr.	MMA m./l.	Polymer ppts., hr.
Pd	24	0.180	14
Pd	12	.106	20
Ni	24	.137 + 10^{-2} *N* HCl	24
Ni	24	.09 + 10^{-2} *N* HCl	30

Results with the apparatus shown in Fig. 1 are recorded in Table III.

When the total amount of chain starters $\overline{N}$ was determined from the total amount of polymer recovered and its viscosity average molecular weight $\overline{M}$ the results showed low efficiencies of

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* Condensed from a paper first submitted for publication September 14, 1949.

[1] Wilson, *Record Chem. Progress*, **10**, 25 (1949).

[2] Kobosew and Nekrassow, *Z. Elektrochem.*, **36**, 529 (1930).

[3] Bodenstein, *ibid.*, **28**, 517 (1922).

[4] Parravano, THIS JOURNAL, **72**, 3856 (1950).

[5] Vanino, "Präparative Chemie," I Band, Ferd. Enke, Stuttgart, (1923).

TABLE III

INTERACTION OF METALS LOADED WITH HYDROGEN WITH MMA AQUEOUS SOLUTION AT 22°

Cathode	MMA m./l.	Turbidity time, hr.	Polymer ppts., hr.
Pd	0.150	~16	~18
Pd	.150	~18	~21
Ni	150 + 10^{-2} *N* HCl	~24	~30

chain initiation. The protocol of single experiment illustrates this point.

Run No. 6.—Cathode Pd foil, thickness 0.001 inch; anode smooth Pt; electrolyte 0.1 *N* H_2SO_4. Compartment B filled with 0.150 *M* MMA. Solution deaerated. Cathodic c.d. = 15 ma./sq. cm., temp. 20°. Turbidity time 12 hr., polymer precipitates in 15 hr. The polymer, PMMA, was filtered, washed, dried at 65° to constant weight. Weight PMMA 0.1154 g., $[\eta]$ 3.58, $\bar{M}$ 1.0×10^6, $\bar{N}$ 6×10^{16}. This value of $\bar{N}$ is to be compared with the number of H^+ discharged $= 0.004 \times 15 \times 3600 \times 0.01 \times 6 \times 10^{23} = 1.3 \times 10^{24}$.

Pd and Ni foils which had not been used as cathodes, or Pd which had been used as anode, when brought into contact with an aqueous solution of MMA gave no polymerization.

In Table IV are recorded the results obtained with Cu and Ti hydrides.

TABLE IV

INTERACTION OF METAL HYDRIDES WITH *ca.* 0.1 *M* MMA AQUEOUS SOLUTION AT 22°

Hydride	Weight (approx.), g.	Medium	Turbidity time, sec.	Polymer ppts., min.
Cu	2	HCl (0.01 *N*)	45	15
Cu	2	HCl (0.1 *N*)	20	5
Ti	0.5	H_2SO_4 (1 *N*)		180

Electrodeposited metals gave the results in Table V.

TABLE V

INTERACTION OF ELECTRODEPOSITED METALS WITH MMA AQUEOUS SOLUTION AT 26°

Metal surface area 2 cm.²	Medium	Turbidity time, hr.	Polymer formed, hr.
Fe	0.180 *M* MMA	?	Traces
Fe	.180 *M* MMA + 0.01 *N* HCl	?	Some after 72
Cr	.180 *M* MMA	~15	24
Co	.180 *M* MMA + 0.01 *N* HCl	18	70

In Table VI are collected the data obtained for the chemisorption of hydrogen on various metal powders or blacks.

TABLE VI

INTERACTION OF METALLIC POWDERS AND BLACKS LOADED WITH HYDROGEN WITH AQUEOUS SOLUTIONS OF MMA AT 24°

Sample ~0.05 g.	MMA m./l.	Turbidity time, hr.	Polymer ppts., hr.
Ni powd.	0.106	2.0	4
Ru powd.	.106	2.5	4
Ni (from NiO)	.106	0.5	2
Pt black	.140	3.0	5.0
Pd black	.140	~3.0	4.0

Discussion

As all these results indicate, initiation of addition polymerization reactions in liquid phase seems to be a general feature of metal–hydrogen systems produced by electrolysis at cathodes or by chemisorption of hydrogen on metals. In this respect, the results are entirely analogous to those previously obtained in the catalytic decomposition of hydrazine and of formic acid at palladium and platinum surfaces.[6]

As with these catalytic reactions the efficiency of the process of initiation is low in terms of total hydrogen produced or present. As shown in Run No. 6 with the apparatus of Fig. 1, this efficiency may be as low as 10^{-7} to 10^{-8}. It is evident that, of the total hydrogen liberated at a cathode surface, the bulk is released as molecular hydrogen. A very minor fraction leaves the surface either as an atom or as a radical by interaction with a monomer molecule and acts as a polymerizing center in the body of the monomer solution. The development of the polymerization process through the stages of turbidity and precipitation is entirely parallel with that obtaining in the catalytic processes of initiation previously reported.[4] It is suggested that the mechanism of polymer growth there discussed is operative in the present experiments also. The precipitate forms through growth of the radical polymer unit by diffusion of monomer units into a particle and reaction there with the radical. In confirmation of such a view is an experiment in which electrolysis of an acid–monomer solution was conducted for an interval of time less than that required to develop visible turbidity. The cathode liquor so prepared was run off from the electrolysis system into a solution of monomer. With progress of time, turbidity and precipitation of polymer developed without further intervention of electrolysis.

The effectiveness of the cathode material was parallel to the overvoltage of the metal as shown in Table I. In this respect the results are parallel to those of Kobosew and Nekrassow[1] using the technique of reduction of WO_3 suspensions and the development of the blue color of the reduced oxide. The present experiments are free from an objection that might have been raised against the WO_3-experiments, namely, that the reduction observed might only be occurring at the contact between the cathode and the oxide which had settled onto it. In the present experiments the chain starter can definitely leave the electrode surface and its presence in the body of the solution is made evident by the formation of solid particles. Indeed, the production of solid polymer in MMA solutions outside the electrolytic cell by inoculation with cathode liquor which does not yet show visible turbidity is proof of the existence of polymerization centers away from the cathode.

Kobosew and Nekrassow identify the active agent in the reduction of WO_3 as atomic hydrogen leaving the cathode surface during the electrolysis. They associate the emission of atoms with the over-voltage on the basis of decreasing energy of binding of the hydrogen atom to the metal surface

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(6) Parravano, THIS JOURNAL, 72, 3856 (1950).

with increasing overvoltage. The escape of atomic hydrogen from the cathode to the MMA solution could result in the formation of a free radical with monomer and hence in polymerization. There is also, however, the possibility that reaction of monomer with atoms on the cathode surface and liberation of a radical to the solution may be involved according to the equation

$$\mathrm{MeH} + \mathrm{m} \rightarrow \mathrm{m}^* + \mathrm{Me}$$

where m^* is the liberated radical. Such a process should occur more readily than the evaporation of an atom of hydrogen by reason of the exothermicity q of the reaction between atomic hydrogen and a vinyl compound to form a radical. The energy quantity in the Boltzmann factor governing the process should be lessened by this amount q.

Acknowledgment.—I wish to express my grateful appreciation and thanks to Professor H. S. Taylor for his continuous interest and advice during the course of this work and for assistance in the preparation of the manuscript for publication.

Summary

Polymerization of methyl methacrylate can be initiated during the electrolytic reduction of aqueous solutions of the monomer. The efficiency of the process increases with increasing overvoltage of the cathode.

Metals loaded with hydrogen, either electrolytically or by processes of chemisorption, initiate polymerization of aqueous solutions of methyl methacrylate.

The efficiency of initiation is low compared with the total hydrogen released by electrolysis or present in the chemisorbed state.

Initiation gives rise to radicals which can continue to add monomer units away from the initiation center and over periods of hours, in the original electrolytic solution or in monomer solutions to which the electrolytic solution is added.

Princeton, New Jersey Received July 24, 1950

[Contribution No. 495 from the Department of Chemistry of Indiana University]

Ultraviolet Absorption Spectra of 2-Substituted 8-Quinolinols

By J. P. Phillips,[1] W. H. Huber,[1] J. W. Chung[1] and L. L. Merritt, Jr.

In connection with an investigation of steric hindrance to chelate formation by substituents in the 2-position of 8-quinolinol[2,3] the ultraviolet absorption spectra of a number of 2-substituted 8-quinolinols were determined, since spectra can frequently be used to indicate the existence of steric hindrance to a planar structure caused by substituents.[4] All the compounds included in this study had been shown to exhibit steric hindrance, or at least hindrance from some source,[5,6] to the formation of a chelate with aluminum.

Information about the structure of these compounds in acid, base and neutral solvents was expected from the determination of their spectra, but in order to narrow down the number of possible structural feature–spectra associations the spectra of the 8-methoxy derivatives of most of these compounds were determined also.

Experimental

The preparation of these compounds has been previously described.[5]

The absorption spectra were determined with a Beckman model DU spectrophotometer from 225 to 400 mμ (unless otherwise indicated) using slit widths such that maxima could be located to the nearest 1–2 mμ. Solutions in the concentration range 10^{-3}–10^{-5} M were generally suitable; all the compounds obeyed Beer's law sufficiently well in this range. The accuracy of the molecular extinctions is estimated to be ±10% or better.

Since the spectra of these compounds were generally quite similar in shape to each other and to 8-quinolinol, graphs of which have appeared in the literature several times,[7,8] it was not considered desirable to present plots of our data here.

Results and Discussion

8-Quinolinol has a planar structure composed of three fused rings, one of them completed through a nitrogen–hydrogen bridge. A steric effect by a group in the 2-position sufficient to inhibit the formation of the bridge would make the third ring no longer co-planar with the quinoline nucleus and the consequent decrease in the number of resonance forms should produce a decrease in absorption and a shift to shorter wave lengths in the spectra. A comparison of 2-methyl-8-quinolinol with 8-quinolinol (Table I) and with 4-methyl-8-quinolinol shows that a shift to shorter wave lengths in the 2-substituted compound occurs in the absorption maxima labeled "4" in the tables, but not in the whole spectrum. Similar effects were noted in the copper chelates of these compounds (Table II). Evidence from spectra for steric hindrance in this case is not obtained.

A definite case of steric hindrance was observed from the spectra of 2-*o*-tolyl-8-methoxyquinoline (Table III); this compound absorbed at shorter wave lengths and less strongly than its meta and para isomers, undoubtedly indicating restricted rotation as in substituted biphenyls.[4] Perhaps because of this hindrance we were unable to pre-

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[1] Abstracted from parts of theses submitted by W. H. Huber and J. W. Chung in partial fulfillment of the requirements for master's degrees, and from a portion of the doctoral thesis of J. P. Phillips.

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[5] Phillips, Elbinger and Merritt, *ibid.*, **71**, 3986 (1949).

[6] Irving, Butler and Ring, *J. Chem. Soc.*, 1489 (1949).

[7] Ewing and Steck, This Journal, **68**, 2181 (1946).

[8] Stone and Friedman, *ibid.*, **69**, 209 (1947).