

On substituting *p*-nitroaniline for aniline, immediate coupling occurred in alkaline solution to yield a red dye, similar in appearance to that obtained with aniline.

2(or 4)-Benzylidene-3-(or 2)-butenothiololactone.—To a solution of 0.2 g. of 2-thienol and 0.5 g. of benzaldehyde in 5 cc. of ethanol was added a drop of concentrated hydrochloric acid. Warming on the steam-bath for five minutes, then steam distillation to remove excess of aldehyde, furnished 0.2 g. of a solid which, on two recrystallizations from ethanol, was obtained as light yellow needles, m. p. 97.5–98.5°. The product was insoluble in alkali.

Anal. Calcd. for $C_{11}H_8OS$: C, 70.19; H, 4.28. Found: C, 70.17; H, 4.34.

This synthesis was repeated by Mr. Hugh J. Anderson, who determined its molecular weight cryoscopically in camphor: found, 191; calcd., 188.

Reaction of 2-Thienol with Bromine.—A solution of a weighed amount of 2-thienol in carbon tetrachloride was treated with a known excess of 0.2 *N* bromine in carbon tetrachloride solution in a closed system at -5° . After momentary mixing, the excess bromine was consumed by the addition of potassium iodide solution, and the resulting iodine titrated with thiosulfate. It was thus found that 0.31 mole of bromine had reacted for each mole of thienol present. An identical experiment using phenol in place of 2-thienol consumed 1.00 mole of bromine per mole of phenol.

Repetition of the experiment with 2-thienol, but at 25° for a reaction period of ten minutes resulted in the consumption of 1.09 moles of bromine per mole of thienol present.

Miscellaneous Reactions of 2-Thienol.—When an aqueous solution of 2-thienol was treated with dilute ferric chloride, a light red color appeared. On standing a red flocculent precipitate gradually formed.

A dilute solution of 2-thienol in 20% potassium hydroxide converted a suspension of cadmium carbonate to the yellow cadmium sulfide within 15 minutes at room temperature.

A dilute solution of 2-thienol in 15% sulfuric acid evolved hydrogen sulfide when warmed on the steam-bath.

Addition of a drop of 2-thienol to 10 cc. of ammoniacal silver nitrate resulted in the formation of a silver mirror within one minute.

The characteristic deep blue color of the indophenin test was generated when 2-thienol in thiophene-free benzene was treated with isatin and sulfuric acid.

Oxidation of 3-Thienylmagnesium Bromide.—A Grignard solution was prepared from 54 g. of 3-bromothiophene,⁹ b. p. 156° , 54 g. of ethyl bromide and 19.5 g. of magnesium in 500 cc. of ether. This was added under nitrogen to a solution of isopropylmagnesium bromide prepared from 50 g. of isopropyl bromide and 10 g. of magnesium in 150 cc. of ether. The resulting mixture was treated with oxygen at $0-10^\circ$ and worked up as previously described for 2-thienol. There was obtained approximately 4 g. of an alkali-soluble, bicarbonate-insoluble liquid having a phenolic odor. Attempts to purify this material by distillation or crystallization were unsuccessful. The crude product gave an immediate bright-red color with dilute ferric chloride. Treatment with diazotized aniline in alkaline solution yielded a red-brown solid product.

Twenty-two grams of 3-bromothiophene was recovered from the original oxidation product.

When a Grignard solution was prepared from 3-bromothiophene as described above and poured on solid carbon dioxide, the yield of 3-thienoic acid was 28%. One-half of the 3-bromothiophene was recovered unchanged.

Summary

A method has been developed for introduction of the hydroxyl function into the thiophene nucleus by oxidation of the thienylmagnesium bromide. 2-Thienol has been isolated and characterized. Its behavior indicates the existence of tautomeric forms. Evidence was obtained also for 3-thienol but it was not isolated as such.

(9) Steinkopf, *Ann.*, **543**, 128 (1940).

EVANSTON, ILLINOIS

RECEIVED JUNE 22, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Polymerization Induced by Catalytic Decomposition of Formic Acid at Platinum Surfaces

BY GIUSEPPE PARRAVANO

In a previous communication¹ it has been shown that addition polymerization reactions of a vinyl monomer can be obtained during the catalytic decomposition of hydrazine solutions at palladium surfaces. This effect has been interpreted in terms of chain reactions, initiated at catalytic surfaces and proceeding in the surrounding liquid medium, away from the initiating center.

A similar mechanism is found to be operative during the heterogeneous catalyzed decomposition of formic acid solutions at room temperature. Polymerization reactions have been observed in an aqueous solution of methyl methacrylate in the presence of formic acid or sodium formate solutions and catalytic surfaces such as platinum, palladium, silver and charcoal. In this communication we present the results obtained

in the more detailed study of the decomposition of formic acid solutions at platinum surfaces.

It is known² that the decomposition of formic acid at metal surfaces involves a dehydrogenation reaction which yields carbon dioxide and hydrogen. At room temperature, however, the catalytic activity of platinum metal is very low, but can be markedly increased by the presence of oxygen.² This may be attributed to strong adsorption of the product hydrogen on the pure metal and its oxidation to water in presence of oxygen. The present work confirms the fact that no significant decomposition of formic acid can be detected at room temperature if oxygen is thoroughly excluded from the system. When oxygen is present, a small fraction of the total decomposition processes gives rise to radicals

(1) Parravano, *This Journal*, **72**, 3856 (1950).

(2) Müller and Schwabe, *Z. Elektrochem.*, **34**, 170 (1928).

which, in presence of a monomer, initiate the polymerization process.

Experimental

Materials.—Formic acid solutions were made by dissolving reagent formic acid (Baker and Adamson) in distilled water, the solutions being standardized by alkali titration. A platinum sol was prepared by adding a stoichiometric amount of 0.57 g./l. sodium hydroxide solution to a 0.1% chloroplatinic acid solution. The resultant solution was heated at 70° and a stream of hydrogen bubbled through for three hours. The black sol showed no presence of Pt^{++} ions, and was very stable. The final solution contained 463 mg. platinum per liter. An electron diffraction pattern of the sol gave the lattice structure of pure platinum, with an average crystallite size of about 150 Å.

Methyl methacrylate (MMA) and acrylonitrile (AN) were used as monomers. They were purified as previously described.¹

Experimental Procedures.—Formic acid decomposition was followed by measuring the amount of gas evolved. A suitable reaction vessel containing a standard solution of formic acid with or without monomer was immersed in a shaking thermostat ($\pm 0.05^\circ$). The vessel was connected by means of glass tubing to a volumetric buret, kept at constant temperature. When the amount of gas collected was plotted vs. time a line could be drawn through the points, the slope of the line being taken as the initial rate of decomposition k_d (mole, liter⁻¹, min.⁻¹).

Polymerization reactions were carried out in a series of test-tubes, each containing the same amount of a standard solution of MMA, formic acid and platinum sol with a total volume of 50 cc. in every case. An approximately constant concentration of oxygen was built up in each sample by shaking it with air before a run in a standard way.

The method used to follow the progress of the polymerization, the recovery of the polymer formed, and the determination of the average degree of polymerization, \overline{DP} , has been already described.¹

Experimental Results. Decomposition of Formic Acid Solutions.—In preliminary runs it was found that no decomposition occurs if the reacting solution is thoroughly freed from oxygen by repeated freezing and evacuation. On the other hand, if air is allowed to diffuse into the solution decomposition sets in. Accordingly, the decomposition of formic acid was measured in solutions which were not subjected to any preliminary degassing.

At constant composition of platinum and temperature (25°) the decomposition of formic acid varied linearly with the concentration of formic acid between 2 and 22×10^{-2} m./l. In solutions which contained 0.058 m./l. of formic acid the decomposition of formic acid varied linearly with the amount of platinum sol employed between 0.9 and 4.6 mg. per 50 cc. of solution.

To ascertain the influence of the monomers on the rate of formic acid decomposition experiments were carried out at 50° with solutions containing 0.220 m./l. formic acid and 2.3 mg. platinum per 50 cc. In the absence of monomer it was calculated that $k_d = 7.0 \times 10^{-4}$ (min.⁻¹, mg. Pt⁻¹, 50.2°). With solutions containing 0.131 m./l. MMA it was found that $k_d = 4.3 \times 10^{-4}$ (min.⁻¹, mg. Pt⁻¹, 50.2°). With solutions containing 0.30 m./l. AN, no gas evolution was observed in 120 minutes. As in the case of hydrazine, therefore, MMA has a minor influence on the velocity of formic acid decomposition. Acrylonitrile, on the other hand, acts as a powerful poison, suppressing the decomposition process.

Polymerization Reactions.—In the course of preliminary runs it was readily evident that no polymerization occurred at 25° in solutions containing formic acid, platinum sol and MMA, which were rigorously degassed using a vacuum technique. Since ready polymerization occurred in solutions which were not submitted to evacuation, polymerization reactions were carried out in stationary reaction systems, using solutions which were shaken with air in

a standard way before starting. With this method induction periods were observed, varying from run to run from 15 to 45 minutes, being in all cases equal for every sample within the same run. In general 4 to 5 measurements were made at each set of conditions. The polymerization rates were quite constant after the induction periods. No polymerization was detected in stationary reaction systems in which acrylonitrile was used as a monomer, even after a period of three months. At constant MMA, 0.075 m./l., and formic acid, 0.110 m./l., concentrations, at 25°, R_p varied linearly with the amount of platinum sol employed between 0.5 and 3.2 mg./50 cc. Under these conditions it was calculated that $R_p = 1.60 \times 10^{-4}$ (± 0.15 a. d.) (m./l., min.⁻¹, mg. Pt⁻¹). The linear relation obtained is assumed to be the result of a surface initiation of the polymerization reaction.

The initial rate of polymerization R_p was found to vary linearly with formic acid concentration at definite rates for each of two monomer concentrations with constant platinum content and temperature. A linear relationship obtains for varying MMA concentration at constant platinum and formic acid content at constant temperature. Figure 1 shows a plot of all the data obtained for R_p as a function of $[\text{HCOOH}] \times [\text{MMA}]$, at constant platinum content. The linear relation between R_p and this product is evident. Experiments were carried out at three different temperatures 18, 25 and 35.5°, giving an over-all activation energy for the polymerization process of 16.7 kcal./mole.

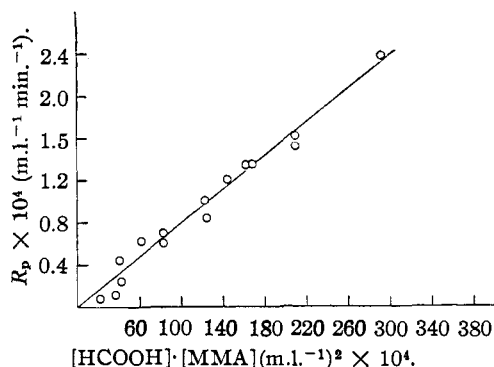


Fig. 1.—Initial rate of polymerization vs. $[\text{HCOOH}] \cdot [\text{MMA}]$; $t = 25^\circ$; $[\text{Pt sol}] = 2.31$ mg./50 cc.

The \overline{DP} of the polymer product was found to be independent of the amount of platinum sol used between 0.9 and 4.7 mg./50 cc. platinum, at constant formic acid concentration, 0.110 m./l., MMA concentration, 0.075 m./l. and temperature, 25°. Under these conditions the PMMA obtained had a $\overline{DP} = (7.7 \pm 0.35) \times 10^3$. The \overline{DP} of the polymer product varied linearly with the initial concentration of MMA. At constant amount of platinum sol, 2.31 mg./50 cc., and temperature, 25°, the \overline{DP} varied from 3.9×10^3 to 11.0×10^3 for 0.110 m./l. formic acid concentration, and from 0.9×10^3 to 3.6×10^3 with 0.220 m./l. concentration of formic acid.

When the \overline{DP} is plotted against the initial concentration of formic acid a linear relation is again obtained. This is shown in Fig. 2 for two different monomer concentrations, at 25°, and 2.31 mg./50 cc. of platinum.

The data obtained serve also to show clearly that this type of surface initiation of a chain polymerization reaction is a process occurring very rarely. A small fraction only of the total number of formic acid molecules which undergo decomposition are used up to produce monomer radicals. This can be seen from the Table I, where, in the last column, are recorded the values obtained for the ratio N_F/N_P , N_F and N_P being the number of formic acid molecules decomposed in presence of monomer, at 50.2°, and polymer molecules formed at 25° per minute, under dif-

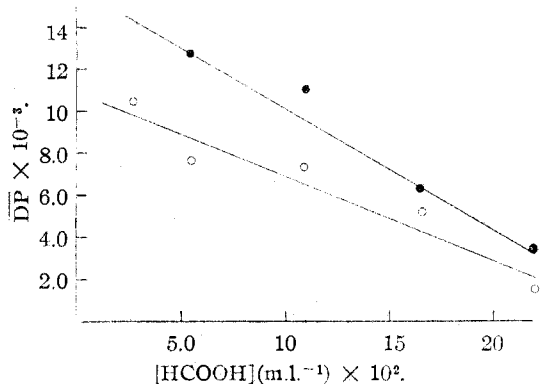


Fig. 2.—The effect of formic acid concentration upon the \overline{DP} of the polymer product [Pt sol] = 2.31 mg./50 cc.; $t = 25^\circ$: O, [MMA] = 0.075 m./l.; ●, [MMA] = 0.131 m./l.

ferent initial concentrations of formic acid, 0.138×10^{-2} m./l. of MMA and 2.31 mg./50 cc. platinum sol. Values obtained for the ratio N_F/N_P are very large, even larger than were found in the case of hydrazine decomposition at palladium surfaces.¹ These values represent the maximum number of polymerization chains which can be obtained for a given number of formic acid molecules decomposed, because, in this calculation, no chain transfer process has been taken into account and the formic acid decomposition in the presence of monomer was measured at 50.2° .

TABLE I

RATIO OF FORMIC ACID DECOMPOSED AT 50.2° IN THE PRESENCE OF MONOMER TO POLYMER MOLECULES FORMED AT 25° WITH [Pt Sol] = 2.31 MG./50 CC.

[MMA] $\times 10^2$, m./l.	[HCOOH] $\times 10^2$, m./l.	Mol. HCOOH dec. per min. $\times 10^{-10}$	Av. PMMA mol. obtained per min. $\times 10^{-14}$	N_F/N_P $\times 10^{-6}$
0.138	2.75	3.3	0.154	2.14
.138	5.5	6.6	0.98	0.67
.138	11.0	14.2	2.92	.48
.138	16.5	21.2	5.0	.42
.138	22.0	28.4	26.8	.107

Discussion

The experimental results are capable of interpretation in the manner already set forth in the case of hydrazine decomposition at palladium surfaces.¹ It is assumed that what is measured is the growth of solid polymer particles containing a free radical by reaction of monomer dissolved in the particle. If it is assumed that the process follows that discussed as Case 2 by Smith and Ewart³ for emulsion polymerization it is evident that

$$R_p = -dM/dt = k_p [M]N/2 \quad (1)$$

where N is the number of growing particles per cc. It is assumed that these growing particles are produced by a reaction between formic acid and the oxygen adsorbed on the platinum surface. The experimental observation that, at constant platinum content

(8) Smith and Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

$$R_p = k[M][\text{HCOOH}] \quad (2)$$

is in best agreement with this view.

The average degree of polymerization, \overline{DP} , is linearly proportional to MMA concentration and inversely proportional to the formic acid concentration. From a plot of \overline{DP}^{-1} vs. MMA^{-1} , shown for two different concentrations of formic acid in Fig. 3, the extrapolation to $\text{MMA}^{-1} = 0$ yields in accordance with the general kinetic treatment for addition polymerization a value for $k_{tr,m}/k_p$, where $k_{tr,m}$ is the specific rate constant for monomer transfer. It is of interest that the value obtained for this ratio is 0.2×10^{-4} in agreement with that previously obtained with hydrazine and also by Matheson, *et al.*,⁴ in the photopolymerization of MMA.

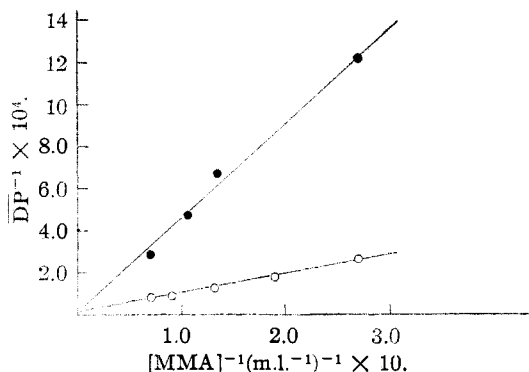


Fig. 3.—Plot $1/\overline{DP}$ vs. $1/[\text{MMA}] \cdot [\text{HCOOH}]$ $t = 25^\circ$; [Pt sol] = 2.31 mg./50 cc.: O, 0.110 m./l.; ●, 0.220 m./l.

From a plot of \overline{DP}^{-1} vs. $[\text{HCOOH}][\text{MMA}]^{-1}$ in Fig. 4 the same value of 0.2×10^{-4} results for \overline{DP}_0^{-1} . The linear plots obtained with varying concentrations of formic acid indicate that chain transfer with formic acid molecules also occurs.

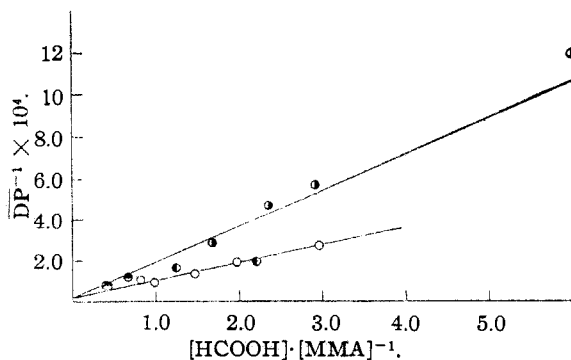


Fig. 4.—Plot $1/\overline{DP}$ vs. $[\text{HCOOH}]/[\text{MMA}]$; $t = 25^\circ$, [Pt sol] = 2.31 mg./50 cc. [HCOOH]: ●, 0.0275 m./l.; ○, 0.0550 m./l.; ○, 0.110 m./l.; ●, 0.165 m./l.; ●, 0.220 m./l.

We shall now discuss the effect of oxygen on the over-all process. From the experimental evi-

(4) Matheson, Auer, Bevilacqua and Hart, *THIS JOURNAL*, **71**, 497 (1949).

dence it can be concluded that: (1) without the presence of oxygen no decomposition of formic acid nor monomer polymerization occurs at room temperature; (2) when oxygen is present in not too large amounts decomposition occurs and polymerization sets in. An induction period is present, and increases with increasing amount of oxygen in the solution; (3) in the presence of large excess of oxygen the decomposition reaction occurs but no ready polymerization can be detected. Therefore, there must be an optimum concentration of oxygen, which gives rise to polymerization with the shortest induction period. This can be explained in the following way. At constant formic acid and monomer concentration the velocity of the initiation step is dependent on the amount of oxygen present on the surface

$$v_i = k_i' [O_2]_{\text{surface}} \quad (3)$$

Under similar conditions the velocity of saturation of polymer radicals by molecular oxygen is

$$v_t = k_t C^* [O_2]_{\text{liquid phase}} \quad (4)$$

Using steady state approximation the velocity of propagation of polymer chains is

$$v_p = k_p \frac{k_i'}{k_t} [M] \frac{[O_2]_{\text{surface}}}{[O_2]_{\text{liquid phase}}} \quad (5)$$

From equation (5) it can be seen that, for low values of $[O_2]_{\text{liquid phase}}$, the metal surface not being saturated with oxygen, polymerization can occur at a measurable rate. As $[O_2]_{\text{liquid phase}}$ increases, the surface saturation is reached, $[O_2]_{\text{surface}}$ becomes constant. The increased concentration

of oxygen in the solution leads however to values of v_p which are too low to be measured.

Acknowledgment.—I wish to express my sincere thanks to Professor H. S. Taylor for his help, advice and criticism during the course of this investigation. E. I. du Pont de Nemours and Company assisted this work through a grant-in-aid to Princeton University, for which assistance best thanks are also extended.

Summary

1. The decomposition of formic acid solutions at the surface of platinum sol in the presence of oxygen and of methyl methacrylate initiates polymerization of the monomer.

2. Acrylonitrile is not polymerized under the same conditions since it poisons the surface for formic acid decomposition.

3. The rate of polymerization is proportional to the amount of platinum employed and to formic acid and monomer concentrations.

4. The average degree of polymerization is directly proportional to monomer concentration, inversely proportional to formic acid concentration and independent of the amount of platinum employed.

5. Kinetic mechanisms to interpret the data have been derived.

6. Only a very small fraction of the decomposed formic acid initiates chain polymerization of the monomer.

7. The effect of oxygen on both formic acid decomposition and polymerization is discussed.

PRINCETON, NEW JERSEY

RECEIVED JUNE 22, 1950

[CONTRIBUTION FROM HOUDRY PROCESS CORPORATION, MARCUS HOOK, PA.]

Chemical Characterization of Catalysts. II. Oxygen Exchange between Water and Cracking Catalysts

BY G. A. MILLS AND S. G. HINDIN

Introduction

The reactions occurring between water and oxides used in petroleum cracking catalysts are of special importance because (1) water is the medium from which oxide catalysts are prepared in hydrogel form, (2) water is normally responsible for loss of activity during catalyst use, and (3) water is believed to be fundamental to the mechanism of the cracking process.^{1,2}

The reactions between water and the surfaces of cracking catalysts were investigated by tracing the reaction with isotopic oxygen. These exchange data have been correlated with ignition loss and surface area determinations, and the results interpreted in terms of the atomic structures of the surfaces involved.

(1) Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947).

(2) Milliken, Mills and Oblad, *Trans. Far. Soc.*, Symposium on Heterogeneous Catalysis, 1950.

While the bulk structure of many solids are known in detail, little experimental evidence is available to establish the surface structure. The measurement of physical properties, although giving valuable information, does not define the chemical nature of the surface, nor does it allow conclusions concerning reactions that may be occurring there. These highly specific surface chemical properties have been widely recognized in colloidal phenomena and particularly in heterogeneous catalysis, and the first paper of this series³ has discussed a chemical characterization of petroleum cracking catalysts through their reaction with basic substances.

Although isotopic tracer methods have been used to elucidate the mechanisms of catalyzed hydrocarbon reactions, most investigators have been concerned with atomic rearrangements in

(3) Mills, Boedeker and Oblad, *This Journal*, **72**, 1554 (1950).