ies of the sulfation which showed that primary alcohols, including neopentyl, sulfated at comparable rates which were about ten-fold faster than the secondary alcohols. The experimentally determined rate law was consistent with the proposed mechanism, and had the form $d(ROSO_3H)/dt = k(ROH)(H_2SO_4)(H^+ \text{ activity})$.

RECEIVED JANUARY 16, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Polymerization Induced by Catalytic Decomposition of Hydrazine at Palladium Surfaces

BY GIUSEPPE PARRAVANO

The problem of the extent to which chemical processes can be initiated at surfaces and can continue in the surrounding medium by a series of chain steps involving atoms and radicals is important not only in respect to the mechanism of chain reactions of combustion but also in the formulation of mechanism in enzymic and biological processes.[1] There is definite evidence for the starting of long reaction chains in gaseous combustion at containing surfaces.[2] There is no systematic body of evidence with respect to the initiation of reactions at solid surfaces acting as catalysts and the propagation of the chains in the surrounding liquid media, away from the initiating surface. Solid aluminum halides and sodium metal as polymerization catalysts constitute exceptions in this respect. It is the object of the present and succeeding communications to indicate that such processes do occur. There are many ways in which polymerizations in liquid media may be initiated by a reaction starting at a solid surface in contact with the liquid medium.[3] The present communication deals with the polymerization of methyl methacrylate induced by the catalytic decomposition of hydrazine sulfate solutions at surfaces of palladium black.

Experimental

Materials.—Hydrazine sulfate solutions were made by dissolving hydrazine sulfate (Paragon Testing Laboratories) in distilled water, the solutions being standardized by titration with potassium bromate in acid solution.[4]

A fine suspension of palladium black was prepared by adding a stoichiometric amount of 2% sodium carbonate solution to a 1% palladium chloride solution. The mixed solutions were heated to 70° and a stream of hydrogen bubbled through for two hours. The precipitate was washed by decantation with six liters of distilled water, filtered and stored under distilled water. The particle size was small enough to permit transfer of a constant quantity of the metal by means of a pipet to the reaction mixture. The final suspension contained 296 mg. of palladium per liter. Examined under the microscope the particles revealed a skeletal aggregated structure of average size 3×10^{-2} cm. During hydrazine decomposition the aggregates are broken up, the resulting particles being round compact structures. An electron diffraction pattern of the freshly prepared suspension gave the lattice structure of pure palladium.

Methyl methacrylate (MMA), acrylonitrile (AN) and methacrylonitrile (MAN) from the Röhm and Haas Company were used as monomers. They were distilled under vacuum before use, the middle fraction, stored in the dark under oxygen-free nitrogen, being used in the experiments.

Experimental Procedures.—The decomposition of hydrazine sulfate solutions was followed in test-tubes. The temperature was controlled to ±0.01° in a thermostat. At intervals samples were removed and analyzed, the hydrazine sulfate decomposed being plotted against time. In the initial stage of the decomposition a linear plot was obtained, whose slope was taken as the initial rate, R_d (mole liter^{-1} min.$^{-1}$), for the decomposition.

The polymerization studies were carried out in a series of test-tubes each containing the same amount of a standard solution of MMA, of hydrazine sulfate and of the suspension of Pd black, with a total volume of 50 cc. in every case. An oxygen-free nitrogen atmosphere was used to deaerate the solutions and was maintained until the test-tubes were stoppered and placed in the thermostat. Reaction was permitted to continue for different intervals of time, the longest time interval being chosen so that not more than 15% of the monomer would be polymerized. After reaction, the tubes were first chilled in ice, opened and their contents filtered, washed on a fritted glass crucible and then dried to constant weight at 70°. The weights recorded were corrected for the weight of palladium simultaneously present in the product.

The different amounts of polymethyl methacrylate (PMMA) obtained in the several time intervals in one series were plotted against time, yielding a straight line plot whose slope was taken as the initial rate, r_p (mole liter^{-1} min.$^{-1}$), of the polymerization reaction.

The average degree of polymerization, $\overline{DP}$, of the polymer products was deduced from viscosity measurements. These were made in a modified Ostwald-type viscosimeter[5] ASTM series #50. Benzene solutions, 0.1 to 0.2% in PMMA were used for the measurements. The equation of Schulz,[6] $[\eta] = \eta_{sp}/c/(1 + 0.30\eta_{sp})$ and of Evans,[7] for unfractionated polymer, $\overline{DP} = 2.81 \times 10^3 [\eta]^{1.32}$, were used in the determination of the viscosity $[\eta]$ and the viscosity average degree of polymerization, $\overline{DP}$. The approximations involved in the use of such data do not, it is believed, invalidate the conclusions to be drawn concerning $\overline{DP}$. The concentration unit for the polymer solution was g. polymer/100 cc. solvent.

Measurements of pH were made with a Beckmann pH meter, using a glass electrode.

Experimental Results

Decomposition of Hydrazine Sulfate Solutions.—At constant concentration of Pd, 4.44×10^{-3} g./50 cc. total solution, at constant temperature 25 ± 0.01° and at con-

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[1] Haber and Willstätter, *Ber.*, **64**, 2844 (1931).

[2] Alyea and Haber, *Z. physik. Chem.*, **10B**, 273 (1930); Mitchell and Marshall, *J. Chem. Soc.*, **123**, 2448 (1923).

[3] Parravano, *Research*, **2**, 495 (1949).

[4] Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

[5] Cannon and Fenske, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 297 (1938).

[6] Schulz and Blaschke, *J. prakt. Chem.*, **158**, 131 (1941).

[7] Baxendale, Bywater and Evans, *J. Polymer Sci.*, **1**, 237 (1946).

stant *p*H = 2.33, the decomposition of hydrazine sulfate varied linearly with the concentration of the hydrazine between 2 and 25 × 10^{-2} moles/50 cc. From the data it was calculated that k_d = 1.69 (min.$^{-1}$ g. Pd^{-1}, 25°).

In solutions which were 0.138 *M* in hydrazine sulfate, at *p*H 2.33 and 25°, the decomposition of hydrazine sulfate varied linearly with the amount of Pd black employed between 2 × and 10 × 10^{-3} g. per 50 cc.

Measurements at 25, 35 and 45° on solutions with the same reactants gave a straight line plot, log initial rate of hydrazine decomposed *vs.* $1/T$, yielding an observed activation energy E = 10.5 kcal./mole.

In order to study the effect of MMA and of AN on the rate of decomposition of hydrazine, measurements were made at 50.3° instead of at room temperatures. The rates of decomposition were determined by measuring the gas evolved per unit of time. With 0.25 *M* hydrazine sulfate solution the initial rate of decomposition was 1 cc. gas per 25 minutes. In presence of 0.112 *M* MMA, 47 minutes were required for 1 cc. evolution. In presence of 0.3 *M* AN no gas evolution was observed in 90 minutes. These experiments show that the presence of MMA approximately halves the rate of decomposition of the hydrazine under the given conditions. The acrylonitrile, however, effectively suppresses the decomposition of hydrazine, presumably because it is strongly adsorbed at the palladium surface and is acting as a powerful poison for the heterogeneous decomposition process.

Polymerization Reactions.—In preliminary runs it was shown that copious polymerization occurred within a few hours with MMA in solution with hydrazine sulfate in contact with Pd black. No ready polymerization occurred with AN or MAN. With the latter, a slight turbidity was noticed after a period of days, but, even after five months, no polymer precipitated out of the solution.

The course of the polymerization process with MMA is interesting to observe. After an interval of time, of the order of ten minutes, in stationary systems a slight turbidity is observed in the layer of liquid immediately above the palladium which has settled to the bottom of the containing vessel. Within a few minutes the turbidity spreads vertically through the column of reaction mixture and opalescence becomes general throughout the solution. The opalescence develops with the formation of a finely divided white precipitate. It is this polymer which is collected, dried and weighed as previously described.

The polymer can form in quantity at long distances from the palladium as can be shown in an interesting experiment.

A cylindrical tube 80 cm. long × 1.4 cm. diameter was attached by a stopcock to another length of tubing 8 cm. long, 2.4 cm. diameter sealed at its base and carrying a side tube inlet. Into the lower compartment a water suspension of palladium black was placed (14.6 mg. Pd) completely filling this up to the stopcock which was then closed. In the upper compartment 80 cc. of a solution 0.15 *M* MMA + 0.275 *M* $N_2H_5HSO_4$ was placed. After the palladium black had settled the stopcock was opened and monomer-hydrazine diffused slowly into the lower compartment. Turbidity resulted just above the sedimented palladium and increased in amount giving a solid polymer which grew and passed through the stopcock bore. When polymer was observed beyond the stopcock, this latter was closed. Polymer continued to form in the upper compartment and the whole 80 cm. length was filled with white solid polymer within a few minutes. These observations are suggestive of growth of solid polymer by diffusion of monomer into the solid polymer phase to add to chains still growing within the solid and far away from the initiating center.

With MMA, a series of polymerizations were carried out in which the reaction mixture was shaken continuously in the thermostat. Only a slight turbidity was detected in the solution after 24 hours in the normal procedure and even with rigorous exclusion of oxygen. No measurable amount of polymer was formed even in two days. If the shaking were discontinued PMMA was formed in measurable quantities in a few hours. Accordingly, experiments on the induced polymerization of MMA were made in stationary reaction systems, in the thermostat, with varying concentrations of reaction constituents. Copious polymerization occurred in all cases in a few hours.

The influence of the amount of Pd black employed is shown in Fig. 1 in which the initial rate of polymerization is plotted as a function of grams palladium employed. A *linear* relation is obtained. This constitutes primary evidence of the initiation of the polymerization process at the surface of the palladium. The reactant concentrations were 0.138 *M* hydrazine sulfate and 0.15 *M* in methyl methacrylate at a *p*H of 2.33.

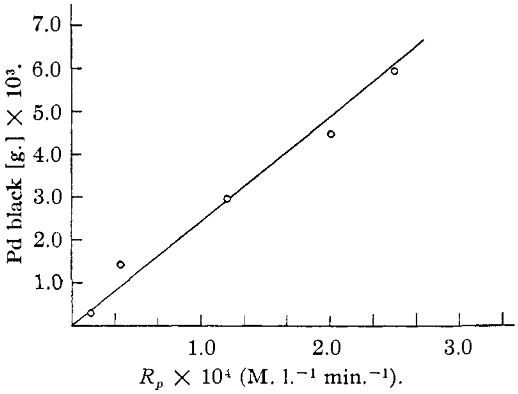

Fig. 1.—The effect of the amount of Pd black on the initial rate of polymerization; MMA = 15 × 10^{-2} *M*; $N_2H_5HSO_4$ = 13.8 × 10^{-2} *M*; *p*H = 2.33; *t* = 25 ± 0.01°.

The influence of hydrazine concentration on the over-all polymerization process is shown in Fig. 2 with two different concentrations of MMA, 4.44 × 10^{-3} g. Pd, *p*H 2.33 and a temperature of 25°. At low concentrations of hydrazine the polymerization varies linearly with the hydrazine concentration but reaches a saturation value at higher concentrations. The curves obtained resemble a Langmuir isotherm.

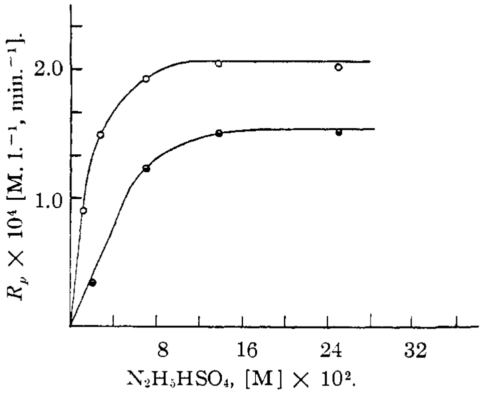

Fig. 2.—The effect of the $N_2H_5HSO_4$ concentration on the initial rate of polymerization; Pd black = 4.44 × 10^{-3} g.; *p*H = 2.33; *t* = 25 ± 0.01°; ○ MMA = 11.24 × 10^{-2} *M*; ● MMA = 5.62 × 10^{-2} *M*.

Similar isotherm-type curves are obtained with varying MMA concentration as shown in Fig. 3. The two curves refer to two concentrations of hydrazine with the same amount of Pd black as in the preceding case, *p*H and temperature also being the same.

If the $\overline{DP}$ be plotted for varying concentrations of MMA at two concentrations of hydrazine sulfate, 0.07 and 0.138

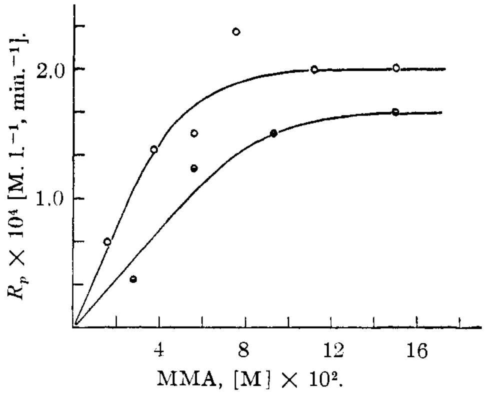

Fig. 3.—The effect of the MMA concentration on the initial rate of polymerization; Pd black = 4.44 × 10^{-3} g.; pH = 2.33; t = 25 ± 0.01°; ○ $N_2H_5HSO_4$ = 13.8 × 10^{-2} M; ● $N_2H_5HSO_4$ = 7.0 × 10^{-2} M.

M, respectively, other conditions being those obtaining in Figs. 2 and 3, a linear relation $\overline{DP}$ *vs.* MMA is obtained in each case.

Figure 4 shows that the $\overline{DP}$ is relatively insensitive to varying hydrazine sulfate concentrations at two concentrations, 0.056 and 0.112 M of MMA, again with other conditions unchanged.

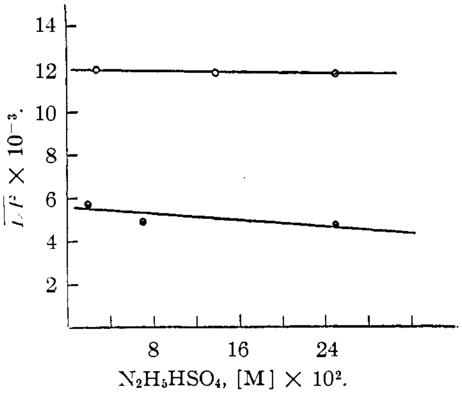

Fig. 4.—The effect of the $N_2H_5HSO_4$ concentration on the degree of polymerization; Pd black = 4.44 × 10^{-3} g.; pH = 2.33; t = 25 ± 0.01°; ○ MMA = 11.24 × 10^{-2} M; ● MMA = 5.62 × 10^{-2} M.

Figure 5 shows that the $\overline{DP}$ is also insensitive to variation in the amount of Pd black employed with constant conditions of hydrazine and monomer concentrations at constant temperature and pH.

Experiments at 16, 25 and 34° gave a straight line relationship between the logarithm of PMMA produced as a function of $1/T$. From the slope of the straight line an observed over-all activation energy of 10.2 kcal./mole was derived.

Experiments at 25° were carried out to ascertain the relationship between PMMA produced and quantity of hydrazine decomposed. From such measurements an estimate could be made of the efficiency of the catalytic decomposition in the initiation of polymerization. Two concentrations of monomer (5.62 and 11.24) × 10^{-2} M were employed and varying concentrations of hydrazine sulfate from 0.138 × 10^{-2} to 2.95 × 10^{-2} M with 4.44 × 10^{-3} g. of Pd in each case. The number of hydrazine molecules decomposed in the absence of monomer and the number of PMMA molecules produced under the same conditions in its presence per unit of time were determined. The latter data were obtained from the weight of polymer product and the average molecular weight as calculated from the viscosity determinations on solutions of the polymer in benzene. The data are shown in Table I. The last column headed N_H/N_P × 10^{-3} gives the ratio of the two molecular quantities. The calculations are only approximate since, as already shown, the presence of monomer cuts down hydrazine decomposition at 50° by a factor of about 2. Also, since the calculations do not take into account any chain transfer processes which increase N_P, the data serve merely to show that only a very small fraction of the decomposition processes lead to chain initiation.

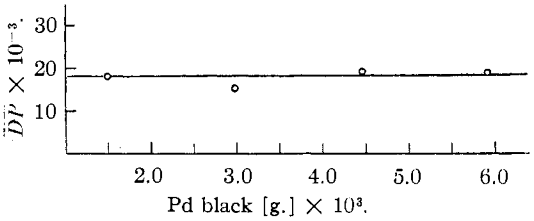

Fig. 5.—The effect of the amount of Pd black on the degree of polymerization; $N_2H_5HSO_4$ = 13.8 × 10^{-2} M; MMA = 15.0 × 10^{-2} M; t = 25 ± 0.01°; pH = 2.33.

TABLE I

RATIO OF HYDRAZINE DECOMPOSED IN ABSENCE OF MONOMER TO POLYMER MOLECULES PRODUCED IN ITS PRESENCE AT 25° WITH 4.44 × 10^{-3} G. Pd

MMA concn. × 10^2 M	Hydrazine concn. × 10^2 M	Molecules hydrazine dec. in absence of monomer per min. × 10^{-18}	Average PMMA molecules formed per min. × 10^{-14}	N_H/N_P × 10^{-3}
11.24	0.138	0.485	2.10	2.3
	0.276	1.82	3.60	5.0
	1.38	6.30	5.05	12.6
	2.50	14.0	5.00	28.0
5.62	0.20	1.09[a]	0.63	17.3
	0.70	3.72[a]	3.10	12.0
	1.38	6.30	4.35	14.4
	2.50	14.0	4.62	32.0

[a] Interpolated values.

Discussion of Results

The significant experimental data are the following: (1) the over-all initial rate of polymerization R_p is dependent on the quantity of palladium employed and (2) on the concentration of hydrazine in solution; (3) R_p is also dependent on the monomer concentration in the solution; (4) the $\overline{DP}$ of the PMMA obtained is linearly dependent on the MMA concentration and only slightly dependent on hydrazine concentration.

The experimental data cited in Figs. 1–3 record the amounts of weighable polymer formed with time between the opalescent phase of the experiment and its termination at a given interval of time. This formation of solid polymer can occur, as has been shown, at large distances from the loci of initiation at the palladium surface. If it is assumed that, in the interval of time during which opalescence develops, a steady state concentration of growing polymer units is established, the interpretation of the data on the basis of chains growing within the solid particles becomes possible. The interpretation would be analogous to that which Smith and Ewart suggest for the kinetics of emulsion polymerization.[8] The present experiments would tend to correspond to their important Case 2, in which "there is no readily available mechanism by which the activity of a free radical in a polymer particle can be transferred to the water phase," the free radical remaining there until another comes to terminate it. Case 2 of Smith and Ewart leads to a very simple formula

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

where [M] is the monomer concentration and N is the number of polymer particles per cc., k_p being the rate of chain propagation. This equation requires that the probability of mutual termination of two free radicals in the same particle is large enough so that the average time necessary for them to terminate is small compared to the average time interval between successive entries of free radicals into a particle. This condition which appears to be observed in emulsion polymerization of styrene is also probable in the present set of experiments.

The equation (1) applied to the present data would indicate that N would be determined by the quantity of palladium employed and the first power of the hydrazine concentration, at least at the lower concentrations of hydrazine employed. The monomer concentration, [M], enters the expression since it governs the amount of monomer available to the growing polymer particle according to the general equation for propagation

$$v_p = k_pC^*[M] \qquad (2)$$

That chain transfer processes are also operative is evident from the data on $\overline{DP}$. The plots of $\overline{DP}^{-1}$ *vs.* $[M]^{-1}$ for two different concentrations of hydrazine solutions shown in Fig. 6 yield good straight lines in each case, which, on extrapolation to $1/[M] = 0$ gives the value $1/\overline{DP}_0 = 0.2 \times 10^{-4}$. From the general kinetic treatment for addition polymerization reactions this extrapolated value is $k_{tr,\,m}/k_p$ where $k_{tr,\,m}$ is the specific rate of transfer between C* and monomer. It is of interest to record that the value for this ratio obtained in the present instance is of the same order of magnitude as that obtained by Matheson, *et al.*, in the photopolymerization of methyl methacrylate.[9] From a plot of $1/\overline{DP}$ *vs.* $[N_2H_4]/[M]$ Fig. 7, the straight lines also extrapolate to a value for $k_{tr,\,m}/k_p = 0.2 \times 10^{-4}$. The data obtained indicate that chain transfer with hydrazine occurs more readily than with monomer, the ratio $k_{tr,\,N_2H_4}/k_{tr,\,m}$ being of the order of 10. Using the value of k_p for methyl methacrylate found by Matheson, *et al.*, equation (1) leads to a value of N of the order of 4×10^{-6}.

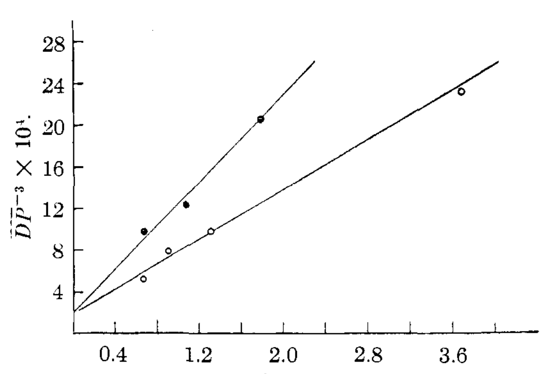

Fig. 6.—Plot $1/\overline{DP}$ *vs.* 1/MMA concentration; Pd black = 4.44×10^{-3} g.; *p*H = 2.33; $t = 25 \pm 0.01°$; ○ $N_2H_5HSO_4 = 13.8 \times 10^{-2}$ *M;* ◒ $N_2H_5HSO_4 = 7.0 \times 10^{-2}$ *M.*

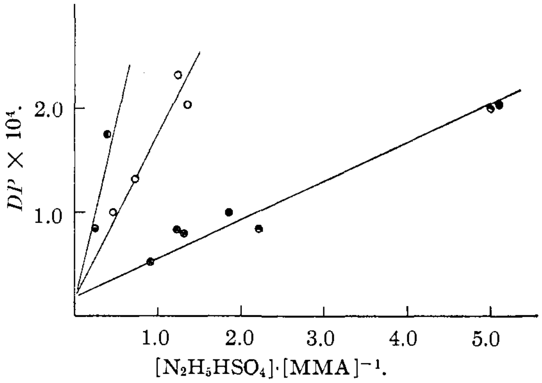

Fig. 7.—Plot $\overline{DP}^{-1}$ *vs.* $[N_2H_5HSO_4]\cdot[MMA]^{-1}$; Pd black = 4.44×10^{-3} g.; *p*H = 2.33; $t = 25 \pm 0.01°$; $[N_2H_5HSO_4]$ ($M \times 10^2$); ◐ = 2.0, ◒ = 2.8, ○ = 7.0, ⊗ = 13.8, ◓ = 25.

On the mechanism here proposed the influence of shaking in decreasing the formation of solid polymer must be associated with a decrease of N in equation (1). This could arise by interaction between a growing polymer unit, probably in the early stages of its growth either with an adsorbed active species on the catalyst surface or by mutual termination of growth by two small growing units assisted by the shaking operation.

Acknowledgment.—I wish to express my sincere gratitude to Professor Hugh S. Taylor, without whose help, advice and criticism this work could not have been carried out. I am indebted also to Professor Arthur V. Tobolsky for discussions on this subject.

Summary

1. The catalyzed decomposition of hydrazine solutions at the surface of palladium black in the presence of methyl methacrylate initiates polymerization of the monomer.

2. Acrylonitrile and methacrylonitrile are not

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

[9] Matheson, Auer, Bevilacqua and Hart, THIS JOURNAL, **71**, 497 (1949).

polymerized under the same conditions, since they act as poisons to the catalytic decomposition of hydrazine.

3. Polymerization is proportional to the palladium employed, to hydrazine and monomer concentrations at low values of these, becoming independent of these at higher concentrations.

4. The degree of polymerization is proportional to the monomer concentration and insensitive to hydrazine concentration and amount of palladium employed.

5. Chain initiation of polymerization occurs in only a very small fraction of the processes of catalyzed hydrazine decomposition.

6. A mechanism involving the growth of solid polymer by interaction of monomer with a free radical within a solid particle has been suggested, the growth being initiated by a reaction at the catalyst surface.

7. Chain transfer processes with monomer and hydrazine are indicated.

8. The experiments show that, under favorable circumstances, chain reactions may be initiated at catalyst surfaces and projected into the surrounding liquid media for propagation.

PRINCETON, NEW JERSEY RECEIVED MARCH 8, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Correction for Free Radicals

BY P. W. SELWOOD AND ROBERT M. DOBRES

Calculations of free radical concentrations from susceptibility measurements involve a correction for the underlying diamagnetism of the free radical. In substituted triphenylmethyls this correction may be comparable in magnitude with the paramagnetic contribution, although, of course, opposite in sign. It is not possible to measure this diamagnetic correction directly, but considerable confidence has nevertheless been attached to the usual methods for estimating the correction. Two methods have commonly been used. These are, first, an application of Pascal's constants and, second, a direct measurement on the corresponding methane, followed by a small correction for one hydrogen. The satisfactory agreement between these two methods is the principal factor which has given confidence in the procedure.

There are in the literature some indications that magnetic measurements sometimes give anomalous results on free radicals. Solutions of the Chichibabin hydrocarbon,[1] although highly reactive and strongly colored, have been reported on the basis of susceptibility measurements, as being not over 2% dissociated to a biradical. But the *ortho–para* hydrogen conversion[2] on solutions of this substance suggest about 10% dissociation. There is also the anomaly that solutions of hexa-*p*-biphenylethane have been shown to be considerably less dissociated,[3,4] on the basis of magnetic measurements, than the pure crystalline solid seems to be. Cryoscopic measurements on this ethane have given contradictory results.[5,6]

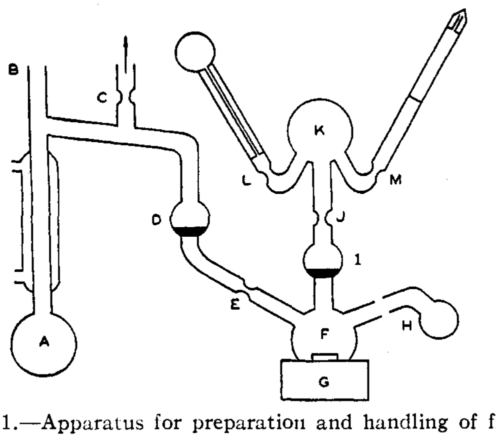

Fig. 1.—Apparatus for preparation and handling of free radicals.

Experimental

Preparation of Materials.—Tri-*p*-biphenylmethyl chloride and tri-*p*-*t*-butylphenylmethyl chloride were obtained through the courtesy of Professor C. S. Marvel of the University of Illinois.

Toluene was extracted with concd. sulfuric acid, washed with water, then with 5% bicarbonate solution, then with water again. It was refluxed over sodium for several hours, then distilled.

Technical pyrene was dissolved in benzene, filtered and twice crystallized.

Solutions of the free radicals were prepared in the apparatus shown in Fig. 1. The apparatus was cleaned, then rinsed with distilled water made faintly alkaline, and thoroughly dried. Toluene and clean sodium slices were introduced into A, which was then cooled to −75°, permitting sealing off at B. The triarylmethyl chloride was placed in F, the molecular silver in a side-arm bulb which was then sealed at H. The toluene was refluxed over the sodium for about one hour. This liquid was cooled to −75° and maintained at this temperature while the entire system was evacuated. The system was sealed off from the vacuum line at C. When A was immersed in tepid water and D, a sintered glass filter, was packed with Dry Ice, the toluene distilled into F which was immersed in a Dry Ice–acetone-bath. A seal was then made at E.

The solute present in F was dissolved with the aid of a magnetic stirrer G. All operations involving the hexaarylethanes were carried out in the dark. Molecular

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[1] Müller and Müller-Rodloff, *Ann.*, **517**, 134 (1935).

[2] Schwab and Agliardi, *Ber.*, **73B**, 95 (1940).

[3] Müller, Müller-Rodloff and Bung, *Ann.*, **520**, 251 (1935).

[4] Marvel, Shackleton, Himel and Whitson, THIS JOURNAL, **64**, 1824 (1942).

[5] Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910).

[6] Bachman and Kloetzel, *J. Org. Chem.*, **2**, 356 (1937).