[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Mechanism of Sulfation of Alcohols[1,2]

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The mechanism of acid-catalyzed esterification of primary and secondary alcohols with carboxylic acids is generally bimolecular with acyl-oxygen fission, in which the alkyl-oxygen bond in the alcohol remains unbroken.[3] We have found that a similar mechanism is probable in the esterification of primary and secondary alcohols with sulfuric acid.[4] Evidence from three sources is presented: sulfation of optically active 2-butanol, sulfation of neopentyl alcohol, and a kinetic study of the rates of sulfation of various alcohols.

Sulfation of Optically Active 2-Butanol

Solutions of *d*-2-butanol in an equimolar[5] amount of sulfuric acid were held at 25° for varying time intervals and then poured into a water suspension of excess barium carbonate. The 2-butanol and barium *s*-butyl hydrogen sulfate were isolated separately and their rotations measured. The results are listed in Table I.

The results in the runs employing 96% sulfuric acid seem best interpreted by assuming that *d*-2-butanol is converted into the acid sulfate with complete retention of configuration, and that the acid sulfate thus produced is rapidly racemized.[6]

TABLE I

OPTICAL ROTATION OF BARIUM *s*-BUTYL SULFATE AND 2-BUTANOL FROM SULFATION OF *d*-2-BUTANOL WITH SULFURIC ACID AT 25°

Time, min.	*s*-Butyl barium sulfate Yield, %	Retention of configuration,[a] %	Retention of configuration in recovered 2-butanol ±0.5%
Equimolar *d*-2-butanol and 96.55% sulfuric acid			
2	2.0	95 ± 4	
5	4.3	83 ± 2	
10	7.7	71 ± 2	
20	13.4	52 ± 2	100
40	17.5	44 ± 2	
105[b]	32	24	
Equimolar *d*-2-butanol and 80.84% sulfuric acid			
60	1.3	65 ± 5	100
120	2.6	63 ± 3	100
200	4.5	61 ± 4	100
300	6.7	58 ± 2	100
600	11.6	51 ± 2	98
Equimolar *d*-2-butanol and 71.44% sulfuric acid			
500	2.2	67 ± 5	100
1200	4.5	59 ± 5	100
Equimolar *d*-2-butanol and 57.44% sulfuric acid			
5760	1.5	59 ± 5	100
100% Sulfuric acid: *d*-2-butanol = 5:1[c]			
0.3	6	99 ± 20	
1.3	20	45 ± 5	
2	8	13 ± 5	
5	2	0 ± 5	

[a] These values are based on the assumption that the *d*-2-butanol and *d*-*s*-butyl hydrogen sulfate have the same configuration (*cf*. Burwell, THIS JOURNAL, **71**, 1769 (1949)). [b] This run is taken from Burwell's data (*ibid*., **67**, 220 (1945)). [c] These runs were conducted at 5–15°. They are in considerable error due to heat effects in mixing.

The fact that the unesterified alcohol isolated from the reaction has completely retained configuration, even after extensive racemization of the *s*-butyl hydrogen sulfate, indicates the the alcohol does not racemize prior to sulfation.

In similar experiments with more dilute sulfuric acid, the highest retention of configuration of the *s*-butyl hydrogen sulfate observed was only 67%. This partial racemization may be the result of the entry of a new non-retention mechanism, possibly the inversion mechanism previously postulated.[7] This mechanism would have to enter to

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[1] This paper was presented at the 116th meeting of the American Chemical Society in Atlantic City, September, 1949.

[2] We wish to acknowledge the generous financial aid of the Office of Naval Research in supporting this work.

[3] This subject has been reviewed by Day and Ingold (*Trans. Faraday Soc.*, **37**, 686 (1941)).

[4] Although tertiary alkyl hydrogen sulfates have frequently been postulated as reaction intermediates, we have been unable to find a record of their isolation either as such or as derivatives. The experiments of Fieser (THIS JOURNAL, **70**, 3232 (1948)) are the most convincing evidence for the existence of tertiary alkyl sulfates, but even in this paper they were not isolated, and the polyfunctional nature of the tertiary alcohols employed leaves doubt as to the exact structure of these sulfated hydroxyquinones. We attempted to secure evidence for the formation of *t*-butyl hydrogen sulfate by adding equal amounts of pyridine-sulfur trioxide to excess *t*-butyl alcohol at 25°. After time intervals ranging from thirty minutes to two days, the solution was poured into water and titrated with 0.5 *N* sodium hydroxide using phenolphthalein as indicator. In each experiment the titer was the same and was that to be expected from pure pyridine-sulfur trioxide. This indicates that either no *t*-butyl hydrogen sulfate was formed, or if formed the hydrolysis was extremely rapid. Similarly by titration technique we could not detect any formation of *t*-butyl hydrogen sulfate when *t*-butyl alcohol and sulfuric acid of various strengths were mixed at 25°. A recent claim for the formation of *t*-butyl hydrogen sulfate (Trink, *Compt. rend.*, **222**, 897 (1946)) was unsupported by experimental evidence. Our observations are in agreement with those of Katsuno (*Bull. Chem. Soc., Japan*, **18**, 267, 211 (1943); *C. A.*, **41**, 4437 (1947)).

[5] Throughout this paper, equimolar refers to the molar ratio of 2-butanol to sulfuric acid disregarding the varying amounts of water present.

[6] The sulfation of *d*-2-butanol, under identical conditions, had previously been interpreted by Burwell (THIS JOURNAL, **64**, 1025 (1942)) as taking place through the carbonium ion, because the acid sulfate obtained was largely racemized. Actually the *s*-butyl hydrogen sulfate isolated after one hundred and five minutes at 25° had a 24% retention of configuration. This agrees with the value expected by extrapolating our data (*cf*. Table I). Burwell (*ibid*., **67**, 220 (1945)) later postulated a carbonium of short life to account for this result. Our view is that the racemization of the *s*-butyl hydrogen sulfate takes place after its formation, and is thus not evidence for the sulfation step especially in the more concentrated acid solutions.

[7] Newman, Craig and Garrett, THIS JOURNAL, **71**, 870 (1949).

the extent of only 15% to account for the observed results.[8]

In these more dilute acid solutions, complete retention of configuration was observed in the unesterified alcohol showing that it was not undergoing a racemization independent of acid sulfate formation.

When a five-fold excess of 100% sulfuric acid was used, the reaction became too rapid to obtain accurate results. However, the *s*-butyl hydrogen sulfate formed with at least a large retention of configuration. Under these conditions the ester rapidly disappeared (*cf.* Table I), and hydrocarbon polymers were the final product.

Sulfation of Neopentyl Alcohol

Whitmore and Rothrock[9] have demonstrated that when neopentyl alcohol is treated with one mole of 96% sulfuric acid, crystalline neopentyl hydrogen sulfate is obtained.[10] On dilute acid hydrolysis neopentyl alcohol was regenerated. The absence of rearrangement provides evidence against a carbonium ion mechanism.

Kinetics of Acid Sulfate Formation

Equimolar quantities of sulfuric acid and various alcohols were held at 25°. The formation of alkyl acid sulfate was followed by adding aliquots to water and titrating with standard alkali. Second order rate constants were calculated from the slope of a plot of the reciprocal of the stoichiometric sulfuric acid concentration, $(H_2SO_4)^{-1}$ (expressed in mols per thousand grams of solution), against time using the data up to 25% toward equilibrium. The basis for assuming rate law 1 is discussed more fully later; however, the qualitative comparison of the rates for various alcohols

$$d(ROSO_3H)/dt = k_2(ROH)(H_2SO_4) \qquad (1)$$

does not depend on the validity of this assumption.

The most striking result is that neopentyl alcohol sulfates at a rate comparable to that of other primary alcohols and pinacolyl alcohol sulfates at a rate comparable to that of other secondary alcohols. Furthermore, primary alcohols sulfate more rapidly than secondary alcohols. A small steric effect is to be noted within each group. The relative rates are in the same order as that found by Menschutkin[11] for the uncatalyzed esterification of alcohols with acetic acid at 150°.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE SULFATION OF ALCOHOLS WITH EQUIMOLAR SULFURIC ACID AT 25 ± 0.1°

Alcohol	Ratio of[a] initial moles, H_2O/H_2SO_4	$K_{eq.}$[b]	Equivalent[c] concentration of aqueous H_2SO_4	Estimated[c] H_0	$k_2 \times 10^7$[d]
2-Butanol	0.194	0.61	82.0	−7.15	147
2-Butanol	0.250		81.8	−7.10	(180)[e]
2-Butanol	0.594	0.49	77.4	−6.41	44
2-Butanol	0.860		74.9	−6.10	(23)[e]
2-Butanol	1.290	0.50[f]	70.4	−5.55	8.0
2-Butanol	2.175	0.29	63.2	−4.70	1.4
2-Butanol	3.980	[g]	52.2	−3.20	0.2
1-Butanol	0.194	2.5[h]	82.0	−7.15	463
Neopentyl	0.194	5.2[i]	82.0	−7.15	367
Methanol	1.290	2.3	70.4	−5.55	69
Ethanol	1.290	1.7	70.4	−5.55	30
1-Butanol	1.290	1.9	70.4	−5.55	20
Isobutyl	1.290	2.2	70.4	−5.55	17
Neopentyl	1.290	1.7	70.4	−5.55	16
2-Propanol	1.290	0.54	70.4	−5.55	8.2
2-Pentanol	1.290	0.64	70.4	−5.55	7.6
3-Pentanol	1.290	[j]	70.4	−5.55	6.7
Pinacolyl	1.290	[j]	70.4	−5.55	3.2
Cyclohexanol	1.290	0.70	70.4	−5.55	11
Methanol	2.175	2.0	63.2	−4.70	13
1-Butanol	2.175	1.7	63.2	−4.70	4.2
Neopentyl	2.175	1.3	63.2	−4.70	4.0
Methanol	3.980	1.3	52.2	−3.20	0.92

[a] The initial moles of alcohol and sulfuric acid were equal. [b] $K_{eq.}$ was calculated from the relation $K_{eq.} = (ROSO_3H)(H_2O)/(ROH)(H_2SO_4)$ and data taken after equilibrium had been attained. [c] The equivalent per cent. sulfuric acid was calculated by assuming that the added moles of alcohol were moles of water. Further assuming that a mole of alcohol will have an effect on lowering the acidity equal to that produced by a mole of water, we can obtain an approximate value of H_0 for these solutions from the tables of Hammett, *et al.* (THIS JOURNAL, **54**, 2721 (1932); **56**, 827 (1934)). It should be emphasized that these estimated values of H_0 are only approximate and do not necessarily remain constant during the reaction. [d] The dimensions of the rate constant are $(\text{seconds})^{-1}$ (mole per thousand grams of solution)$^{-1}$. The precision is ± a unit in the second significant figure. [e] These values are calculated from the total rate of racemization data of Burwell as explained in the discussion section. [f] Robey (*Ind. Eng. Chem.*, **33**, 1076 (1941)) has studied this equilibrium, and shown that it can be attained starting with either the alcohol or olefin. [g] The rate was too slow to estimate $K_{eq.}$ [h] Suter and Oberg (THIS JOURNAL, **56**, 677 (1934)) obtained a value of 2.69. [i] This value is only approximate since crystals appeared before equilibrium was completely attained. These crystals had been reported by Whitmore and Rothrock (*ibid.*, **54**, 3431 (1932)) and are presumably neopentyl acid sulfate. [j] Hydrocarbon formation prevented attainment of equilibrium.

The fact that even in the most favorable examples the sulfation reaction was only 65% complete at equilibrium prevented a critical test of rate law 1 from our kinetic data. However, with the majority of alcohols used the data was sufficient to indicate that second-order kinetics (rate law 1) were preferable to first-order kinetics. For example rate law 1 requires a plot of time against

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(8) With equimolar *d*-2-butanol and 80.84% sulfuric acid, one can account for the results in Table I in an approximate manner by assuming that 1.3% acid sulfate forms each hour, 5% of the optically active acid sulfate racemizes each hour, and that 85% of the acid sulfate forms with complete retention and 15% with inversion of configuration. This type of calculation will be valid only in the early stages of the reaction.

(9) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

(10) We have checked this reaction and estimate by titration a 67% yield of ester at equilibrium at 25° (about ten hours required to reach equilibrium).

(11) Menschutkin, *Ann. chim.*, [5] **20**, 289 (1880). The order of decreasing rates was: methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-butanol and 3-pentanol.

$(H_2SO_4)^{-1}$ to be linear in the early stages of the reaction up to about 25% toward equilibrium, and this was found to be true for all the alcohols studied. In addition it was possible to obtain appreciable rates of sulfation using 100% sulfuric acid in a five-fold excess of methanol. The data in Table III indicate that a first order rate in respect to stoichiometric sulfuric acid concentration is approximated in agreement with rate law 1.

TABLE III

SULFATION WITH 100% SULFURIC ACID IN FIVE-FOLD EXCESS OF METHANOL

Time, hr.	(H_2SO_4) moles/1000 g. solution	% Completion	$k_1 \times 10^5$ sec.$^{-1}$
0	3.94	0	
2	3.31	16	2.5
4	2.80	29	2.4
6	2.41	39	2.3
8	2.08	47	2.2
10	1.84	53	2.1

The slopes of the straight lines obtained by plotting the rate of sulfation of 1 and 2-butanol, methanol, and neopentyl alcohol against H_0 (estimated by the method explained in Table II, footnote[c]) were nearly unity (Fig. 1). Thus rate law 1 can be replaced by the more general rate law 2.

$$d(ROSO_3H)/dt = k(ROH)(H_2SO_4)(H^+ \text{ activity}) \quad (2)$$

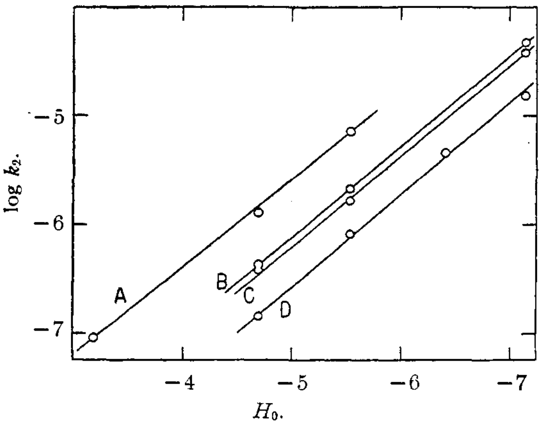


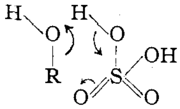
Fig. 1.—Dependence of the rate of sulfation of alcohols on the acidity as measured by H_0: A, methanol; B, 1-butanol; C, neopentyl alcohol; D. 2-butanol.

Discussion

Five mechanisms were considered to be *a priori* possible for the sulfation. The symbols used to denote the various mechanisms are those used by Day and Ingold[3] in a discussion of esterification with carboxylic acids with the exception of S_{N_i} which was introduced earlier for substitution reactions.[12] We have extended these symbols to esterification involving sulfuric acid, as follows.

A″1 $R^+ + HSO_4^- = ROSO_3H$

A″2 $H_2{}^+OR + SO_4H^- = ROSO_3H + H_2O$

S_{N_i}  $= ROSO_3H + H_2O$

A′1 $ROH + SO_3$ (or SO_3H^+) $= ROSO_3H$ (or $ROSO_3H_2{}^+$)

A′2 $ROH_2{}^+ + H_2SO_4 = ROSO_3H + H_3O^+$
$ROH + H_3SO_4{}^+ = ROSO_3H + H_3O^+$
$ROH + H_2SO_4 = ROSO_3H + H_2O$

(This last form falls into this classification if the bisulfate anion is considered as the acid to be esterified.)

The A″1 mechanism involving carbonium ion formation as the rate determining step is ruled out on the basis that it predicts that secondary alcohols would react faster than primary alcohols, and that the acid sulfate would be extensively racemized. Both predictions are contrary to the observed facts. The observation that neopentyl alcohol sulfates without rearrangement is likewise consistent with the absence of a carbonium ion intermediate.

The A″2 mechanism is ruled out on the basis that it predicts inversion of configuration instead of the retention observed. Since the halogen in neopentyl halides is extremely inert to reaction by inversion mechanisms,[13] one would expect the hydroxyl group to be similarly unreactive. Actually neopentyl alcohol sulfated at a rate comparable to other primary alcohols. The analogous situation obtained with pinacolyl alcohol and the other secondary alcohols.

Comparatively little is known concerning the S_{N_i} mechanism. It is hoped that experiments with labelled oxygen can be performed which will critically test this mechanism, which would require oxygen interchange on the alkyl group.

Mechanism A′1 is consistent with the comparative rates of sulfation data and the retention of configuration observed. However, in order to derive rate law 2 from this mechanism, it would be necessary to postulate that the rate of reaction of sulfur trioxide with alcohol was rate-determining rather than the dissociation of sulfuric acid to sulfur trioxide. This seems improbable at the present time.

Most probable is mechanism A′2, which is consistent with the comparative rates of sulfation and the retention of configuration. This mechanism would also account for the terms involving the concentrations of sulfuric acid and alcohol in rate law 2. The relation of mechanism A′2 to the $[H^+]$ term in rate law 2 is more complicated. It depends not only on which of the three forms of A′2 operates, but also on the relative basicities of water and alcohol. We feel that any decision between the three forms of mechanism A′2 must await further work.

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[12] Cowdrey, Hughes, Ingold, Masteramn and Scott, *J. Chem. Soc.*, 1267 (1937).

[13] Hughes, *Trans. Faraday Soc.*, **37**, 620 (1941); Whitmore, Wittle and Popkin, THIS JOURNAL, **61**, 1586 (1939).

Indirect Determination of Rate of Sulfation

It is evident from Table I that after the formation of *s*-butyl hydrogen sulfate with retention of configuration, a rapid racemization follows. Burwell[6] had measured a rate of racemization of *d*-2-butanol by allowing equimolar quantities of alcohol and sulfuric acid to react for varying lengths of time. The alcohol obtained by hydrolysis of the acid sulfate and the alcohol which had not been esterified were combined and the rotation of the mixture measured. The measurements were made after such a time that the concentration of sulfuric acid approached closely to that existing at equilibrium. Under these conditions there will still be considerable optical activity in the free 2-butanol. We now consider Burwell's first order rate constants for the rate of racemization as actually the second order rate constants for sulfation at constant equilibrium concentrations of sulfuric acid. This follows since Burwell's rate is the sum of the rates of sulfation plus racemization, and the sulfation is the slow step. The sulfation rate constants, which can be calculated by the following equation, appear in Table II (*cf.* footnote *e*).

k_2 = Burwell's k_1/equilibrium concentration of H_2SO_4

The agreement with our directly determined rate constants is consistent with this interpretation.

Experimental

Rates of Sulfation.—The procedure was identical to that of Suter and Oberg.[14] The reaction was followed by titrating in diluted aliquots the stoichiometric decrease in acidity as dibasic sulfuric acid was converted to monobasic alkyl acid sulfate. The stability of the end-points showed that hydrolysis of the acid sulfates during titration was negligible. In starting a run care was taken to add the sulfuric acid to the alcohol below 20°. With the three solid alcohols, it was necessary to add small amounts of sulfuric acid at higher temperatures with good stirring until the freezing point of the solution fell below 20°.

Sulfation of *d*-2-Butanol with Sulfuric Acid.—In this work the *d*-2-butanol employed had $[\alpha]^{25}\mathrm{D}$ +11.58°. After the *d*-2-butanol–sulfuric acid solution had stood at 25° for the specified time, it was poured into 200 cc. of water containing an excess of barium carbonate. The slurry was filtered, and the filtrate was concentrated *in vacuo* at 30–40°. Both operations were conducted with a Dry Ice trap in the vacuum line. The contents of the Dry Ice trap were distilled to recover unreacted *d*-2-butanol. The concentrated solution of barium *d*-*s*-butyl sulfate was filtered and the optical rotation observed. It was necessary to use gravity filtration through a very fine filter paper in order to remove the colloidal suspension of barium sulfate which otherwise prevented polarimeter readings.

When the *d*-2-butanol, $[\alpha]^{25}\mathrm{D}$ +11.58, was equilibrated with saturated aqueous potassium carbonate solution[6] the wet *d*-2-butanol had an actual rotation in a 1-dec. tube of +9.03. When this wet *d*-2-butanol was dried over Drierite for three days, the specific rotation returned to its original value of +11.58. In determining the per cent. retention of configuration in the recovered 2-butanol, the aqueous 2-butanol from distillation was dried over excess potassium carbonate at 25°. The observed rotation was compared directly with the value +9.03.

For the specific rotation of completely resolved barium *d*-*s*-butyl sulfate, we used +10.53. This value can be calculated from Burwell's data if the best value, +13.87,[15] is used for the specific rotation of *d*-2-butanol. We also obtained barium *d*-*s*-butyl sulfate, $[\alpha]^{25}\mathrm{D}$ +10.53 ± 0.04, by preparing it from nearly completely resolved *d*-2-butanol and pyridine–sulfur trioxide at 25°, in place of the dioxane–sulfur trioxide originally used by Burwell.[6] Recently Burwell[16] described sulfation of *d*-2-butanol with either sulfamic acid–pyridine or pyridine–sulfur trioxide at 100°, and further confirmed the specific rotation originally published.

Barium and Lithium *d*-*s*-Butyl Sulfates.—Burwell's method[14] appears to be superior to the following method which we used for the preparation of *d*-*s*-butyl sulfates. A mixture of 8.2 g. of *d*-2-butanol ($[\alpha]^{25}\mathrm{D}$ +11.30), 0.5 cc. of pyridine, and 16.4 g. of pyridine–sulfur trioxide (equimolar amount) was stirred for twenty minutes at 25°. The slurry was poured into 100 cc. of water and an excess of aqueous barium hydroxide was added. The mixture was kept at 25° for forty minutes. This alkaline hydrolysis was necessary to completely free the product from chemically bound pyridine. It is suspected that the pyridine is held in the form of anhydropyridinium *s*-butyl sulfate ions ($ROSO_2$-py$^+$). An excess of carbon dioxide was added to precipitate the excess barium. The mixture was filtered. From this solution was isolated barium *d*-*s*-butyl sulfate, $[\alpha]^{25}\mathrm{D}$ +10.53 ± 0.04 (corrected to completely resolved *d*-2-butanol). The solution was carefully treated with an exact equivalent of lithium sulfate solution. The barium sulfate was removed by filtration, and the clear solution evaporated to dryness *in vacuo*. After drying *in vacuo* at 25° to constant weight, the lithium *d*-*s*-butyl sulfate monohydrate weighed 5.63 g. (32% yield based on *d*-2-butanol). The lithium analysis was conducted by oxidizing the corresponding acid sulfate with hot nitric and sulfuric acid followed by ignition to about 700°, and weighing as lithium sulfate.

Anal. Calcd. for $C_4H_9O_4SLi\cdot H_2O$: Li, 3.90. Found: Li, 3.89.

When a slurry of 1.1 g. of *d*-2-butanol, 1.0 cc. of pyridine, and 5.0 g. of pyridine–sulfur trioxide was stirred for one hour at 25°, the yield of barium *d*-*s*-butyl sulfate was nearly quantitative, but some racemization occurred.

When an excess of *d*-2-butanol (3.0 g.) and 1.0 g. of pyridine–sulfur trioxide was stirred for fifteen minutes, the barium *d*-*s*-butyl sulfate could be prepared directly by adding the clear solution to water containing an excess of barium carbonate in suspension. Apparently the RO-SO_2-py$^+$ ion either did not form or was decomposed by the excess of 2-butanol. The barium *d*-*s*-butyl sulfate prepared by this method gave $[\alpha]^{25}\mathrm{D}$ +10.8 ± 0.2 (corrected to completely resolved *d*-2-butanol). The concentration of barium *d*-*s*-butyl sulfate was determined in all cases by converting an aliquot to barium sulfate.

Summary

Evidence is presented to show that esterification of sulfuric acid by primary and secondary alcohols to form alkyl acid sulfates proceeds predominantly by a bimolecular displacement reaction with no alkyl-oxygen fission. The mechanism is similar to the usual acid-catalyzed esterification of carboxylic acids.

The evidence for this mechanism has been obtained from three sources. (1) A study of the sulfation of optically active 2-butanol in which it was shown that the sulfation proceeded with essentially complete retention of configuration. An added complication arose because the *s*-butyl hydrogen sulfate rapidly racemized under the reaction conditions. (2) The demonstration by Whitmore and Rothrock[9] that neopentyl alcohol sulfated without rearrangement. (3) Kinetic stud-

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[14] Suter and Oberg, THIS JOURNAL, **56**, 677 (1934).

[15] Pickard and Kenyon, *J. Chem. Soc.*, 49 (1911).

[16] Burwell, THIS JOURNAL, **71**, 1769 (1949).

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 $d(ROSO_3H)/dt = k(ROH)(H_2SO_4)(H^+ \text{ activity})$.

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[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 *p*H were made with a Beckmann *p*H 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).

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