The Effect of Potassium Persulfate on the Reactions of 2-Butanol in Sulfuric Acid[1]

GEORGE S. CLARK AND JAMES L. WOLFHAGEN*

Department of Chemistry, University of Maine, Orono, Maine 04473

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An investigation of the formation and reactions of *sec*-butyl hydrogen sulfate in H_2SO_4 and D_2SO_4 at 0° was carried out. Either 2-butanol or 2-butene will dissolve in 98% H_2SO_4 (mole ratio 1:5) to form a stable mixture of *sec*-butyl alkoxonium ion and *sec*-butyl hydrogen sulfate if small amounts of $K_2S_2O_8$ are present. The proposed role of $K_2S_2O_8$ as a polymerization inhibitor is that of a scavenger of the traces of 2-butene in the system, thus blocking the initial step of the polymerization reaction, which is assumed to be the addition of *sec*-butyl cation to butene. *n*-Butane was formed in the presence of hydride donors such as methylcyclopentane, indicating the presence of 2-butyl cations in the system. When D_2SO_4 was used, incorporation of carbon-bound deuterium occurred, mostly at C-3, even when $K_2S_2O_8$ was used. It is proposed that H–D exchange occurs in a species which is formed prior to butene in the reaction sequence, and that the intermediate may be a π complex. Nmr spectra at two stages in the conversion of 2-butanol to 2-butylsulfuric acid are presented.

The reaction of simple alcohols and alkenes in sulfuric acid to produce alkylsulfuric acids is well known.[2-6] *sec*-Butyl alcohol also forms the ester, but after a short time, depending on acid strength and temperature, may begin the process of conjunct polymerization, which is the formation of acid-insoluble saturated and unsaturated hydrocarbons together with a series of stable acid-soluble cyclic allylic cations which are recoverable from the acid layer as cyclic hydrocarbons of varying complexity.[7-10]

The reaction may be followed by quenching and weighing of samples removed from the reaction mixture followed by titration of the samples with base. Formation of 1 equiv of $ROSO_3H$ corresponds to the disappearance of 1 equiv of titratable acid.

When the mole ratio of 2-butanol to 96–98% sulfuric acid is 1:5, and at 0°, 2-butylsulfuric acid builds up rapidly in the reaction mixture, reaching a maximum in 40–45 min at 60–70% of the theoretical amount of ester. By this time, the presence of polymer is clearly visible as oily droplets in quenched samples. Polymerization then proceeds rapidly, as indicated by reappearance of titratable acid in successive samples. At the same time the precision of the titration decreases because of the increasing heterogeneity of the mixture owing to the increasing amount of polymer present and the accompanying sampling difficulties.

If, however, a small amount of $K_2S_2O_8$ (0.25 mol % based on the alcohol used) is added to the chilled sulfuric acid just prior to addition of the alcohol, followed by like portions about every 15 min thereafter, the alkylsulfuric acid solution is stabilized against the polymerization reaction without any significant loss of material from the 2-butyl system. Polymer-free systems have been maintained routinely for over 2 hr, using a total of 2 mol % $K_2S_2O_8$. In one experiment, the system was maintained for over 7 hr without visible signs of polymerization by addition of a total of 7 mol % $K_2S_2O_8$. It was noted that excess persulfate was present when the mixture was quenched. Figure 1 shows titration results for composites of several experiments with and without potassium persulfate. Some variation between experiments is observed, but the general form of the curves shown is highly reproducible. The exact shape of any curve is dependent on the strength of acid used. Also, for those experiments in which $K_2S_2O_8$ was used (E-1 and E-2 in Figure 1), additional acidity was continually being produced through the oxidizing action of the persulfate. Accurate corrections could not be made readily for this effect, but they should be small. In spite of some variation in exact shape of the curves for similar reactions run at different times, there is no question about polymerization in the absence of $K_2S_2O_8$, and polymerization inhibition in its presence. The steady-state concentration of alkylsulfuric ester in these experiments appears to lie between 80 and 90% of the theoretical amount. This concentration range is approached when the experiment is begun with butanol and sulfuric acid or with equivalent amounts of butene, water, and sulfuric acid. It seems probable that the apparent steady-state concentration approximates an equilibrium concentration.

The conjunct polymerization reaction also can be observed by noting the appearance of absorption bands in the nmr spectra of the reaction mixtures. These are attributed by Deno[10] to the formation of cyclopentenyl cations. This method is much less sensitive for observing early stages of the reaction than is the observation of these same species by means of their absorption in the ultraviolet at about 305–310 mμ. When potassium persulfate is present, both of these criteria for the onset of conjunct polymerization are absent.

An intriguing feature of the action of $K_2S_2O_8$ on the system 2-butanol–sulfuric acid was the need for continuous addition of the persulfate. When the initial addition of $K_2S_2O_8$ was delayed until 20 min after mixing the alcohol and acid, the alcohol polymerized, and a curve very similar to E-3 in Figure 1 resulted. In other experiments, addition of persulfate was terminated after 45 min. The results of these experiments, when plotted, gave a curve that was similar to E-1 in the initial stages, but the concentration of ester reached a maximum at about 60 min, and then dropped rapidly as in E-3 of Figure 1. When all of the persulfate was added initially, there was some stabilization, but the

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[1] Abstracted in part from the Ph.D. Thesis of George S. Clark, University of Maine, 1968.

[2] C. M. Suter and E. Oberg, *J. Amer. Chem. Soc.*, **56**, 677 (1934).

[3] (a) R. L. Burwell, Jr., *ibid.*, **64**, 1025 (1942); (b) *ibid.*, **71**, 1769 (1949).

[4] R. Robey, *Ind. Eng. Chem.*, **33**, 1076 (1941).

[5] M. S. Newman, *J. Amer. Chem. Soc.*, **63**, 2431 (1941).

[6] A. Tian, *C. R. Acad. Sci.*, **228**, 922 (1949); *Chem. Abstr.*, **56**, 9494 (1950).

[7] V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1936). The general nature of the acid-soluble species, as well as the highly unsaturated character of the acid-insoluble products, appears to have been first recognized by these authors.

[8] W. Calkins and T. D. Stewart, *J. Amer. Chem. Soc.*, **71**, 4144 (1949).

[9] N. C. Deno and M. S. Newman, *ibid.*, **72**, 3852 (1960).

[10] N. C. Deno, D. Boyd, J. Hodge, C. Pittman, and J. Turner, *ibid.*, **86**, 1745 (1964).

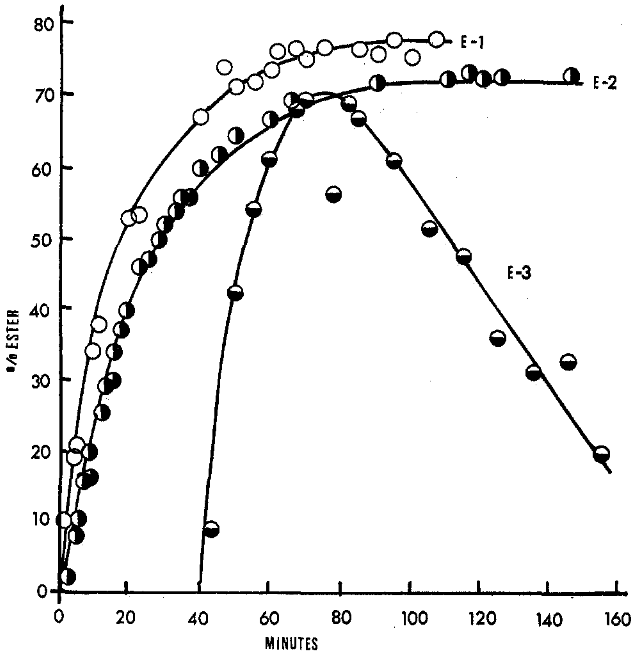


Figure 1.—Esterification of 2-butanol with sulfuric acid: E-1, with 98.1% acid plus $K_2S_2O_8$; E-2, with 95.6% acid plus $K_2S_2O_8$; E-3, 98.1% acid, $K_2S_2O_8$ absent. E-1 and E-2 are composites of two experiments, E-3 of four. The mole ratio of acid/alcohol was 5.0 in all runs. E-3 was displaced 40 min for clarity.

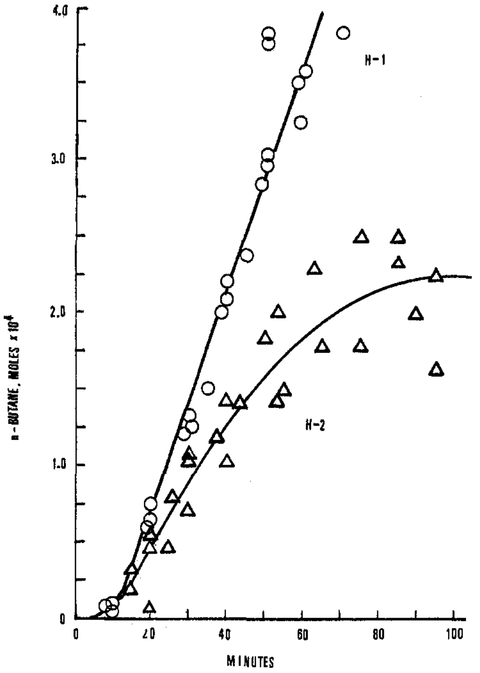


Figure 2.—Evolution of *n*-butane from esterification mixtures in presence of methylcyclopentane: H-1 with $K_2S_2O_8$; H-2 without. Both curves are composites of several experiments.

concentration of ester reached a maximum at 55 min, after which titratable acid reappeared as in unprotected mixtures. The requirement that a small portion of the persulfate be added at regular intervals rather than all of it initially suggests that the persulfate is being used up by a secondary reaction not necessarily related to its inhibiting action on polymerization.

Several experiments were carried out to help decide what step or intermediate in the polymerization reaction was being affected by the persulfate. The rate of alkylation of toluene by 2-butanol–sulfuric acid remained unchanged in the presence of persulfate. Persulfate did not prevent rapid racemization of optically active 2-butanol.[3a,9]

The presence of persulfate did not decrease the apparent initial rate of evolution of *n*-butane in the presence of small amounts of methylcyclopentane or methylcyclohexane (Figure 2), and the rate remains constant through the first hour (curve H-1). The apparent rate of evolution of butane from the system without $K_2S_2O_8$ drops off rapidly as polymerization sets in, presumably because the butane dissolves in the polymer, and its vapor pressure is lowered. This effect could be duplicated by the addition of a relatively large volume of cyclopentane or of inert hydrocarbon.

No isobutane is produced by the mixtures stabilized by persulfate. This is not really surprising, as the evolution of isobutane from unprotected mixtures is part of the complex process of conjunct polymerization.[8]

Because all of these reactions, alkylation, racemization, and butane formation, are believed to involve the 2-butyl cation, it seemed evident that this species was not being affected by the persulfate. These results could have been expected, as carbonium ions are formed relatively rapidly in this system, if the rate of racemization is taken as evidence. Although we have no direct measurement on the rate of racemization, it may be deduced from the combined data of Table I and Figure 1 that about 90% of the alcohol has been racemized in 30 min, for the concentration of ester at this time is about 60% of the theoretical amount, and essentially all of the ester has been racemized. Additionally, approximately 75% of the free alcohol, or another 30% of the total, is racemic. If the *sec*-butyl cation is formed rapidly, then its reaction with small amounts of persulfate could not be the step at which the polymerization reaction is stopped, for the persulfate would be used up rapidly, and the polymerization reaction then could proceed as usual.

TABLE I

RELATIVE NUMBERS OF EXCHANGED PROTONS IN 2-BUTANOL[a] AND RETENTION OF OPTICAL ACTIVITY

	Free 2-BuOH		2-BuOH from ester	
Position	Run D-1	Run D-2	Run D-1	Run D-2
C-1[b]	0	0.3	0.2	0.2
C-2	0.27	0.19	0.61	0.55
C-3	1.00	0.93	1.53	1.55
C-4[b]	0	0.3	0.3	0.1
Retention of optical activity	37%	26%	<1%	<1%

[a] Recovered from solution in D_2SO_4 in presence of $K_2S_2O_8$.
[b] C-1 represents the methyl group adjacent to the carbinol group. The small fractions of protons exchanged on C-1 and C-4 may not be real, but may result from difficulties in choosing a cutoff for the integrations in a region of the spectrum where signals overlapped. For the starting alcohol, $[\alpha]^{25}D$ was +8.80. Time of contact with D_2SO_4 (98%; 5:1 mole ratio of acid to alcohol) was 30 min at 0°.

The most reasonable initial step in the polymerization reaction is the addition of a cation to an alkene. Beyond the initial step the details become lost in a maze of rearrangements, hydride transfers, alkylations, and dealkylations. The formation of 2-butene in the system under consideration must be relatively slow at low temperature, for the amounts of persulfate used to stabilize 2-butanol in sulfuric acid will not stabilize freshly prepared solutions of 2-butene in sulfuric acid unless special precautions are taken which will be discussed shortly. Similarly, when a small amount of *tert*-butyl alcohol is added to a mixture of acid and 2-butanol that is being stabilized, polymerization occurs in spite of continued addition of persulfate. The tertiary alcohol appears to dehydrate so much more rapidly than the secondary alcohol that the persulfate cannot cope with the alkene produced. Also, perhaps the branched structure of the isobutylene produced slows down its possible reaction with persulfate relative to its reaction to form polymer. If alkene can be scavenged from the system as rapidly as it is formed, then the progress of the polymerization is stopped in its initial stage. We have considered that the effect of the persulfate was to oxidize the butene to a glycol, which then might be dehydrated to 2-butanone. Traces of 2-butanone have been detected by comparison vapor-liquid chromatography in a fraction obtained by quenching and neutralizing the reaction mixture, followed by distillation of the volatile organic materials through an efficient column.[11]

Recently, a note has appeared which confirms our supposition that the persulfate may react with alkene. Deno and coworkers[12] have shown that significant yields of glycols may be obtained from appropriate precursors, including 2-butanol, and potassium persulfate in sulfuric acid.

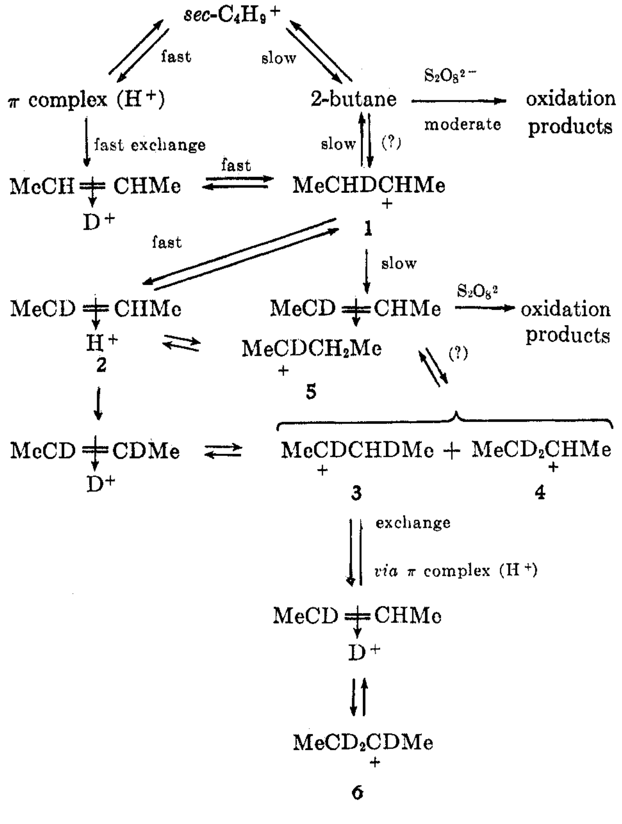
The proposed mechanism for the action of potassium persulfate as an inhibitor of polymerization suggests that the incorporation of carbon-bound deuterium into the molecule might be eliminated, or at least severely inhibited, by the presence of persulfate. Presumably such deuterium incorporation occurs *via* addition of D^+ from D_2SO_4 to alkene. If persulfate removes alkene as fast as it is formed, then deuterium incorporation could not occur. When 2-butanol was allowed to react with D_2SO_4 in the presence of potassium persulfate and then recovered, there was still extensive substitution by deuterium. This result is inconsistent with a mechanism requiring exchange at the alkene stage, but is consistent with a species which can exchange protons with the solvent, and which exists either as an intermediate between cation and alkene or builds up in some branching reaction. Dewar first proposed a species which was represented as a π complex.[13] Taft and coworkers,[14] and others,[15] have suggested such an intermediate from studies on the hydration of isobutene and on oxygen exchange rates for tertiary alcohols in acidic media.

We have considered the possibility that our data do not require the π complex, and that exchange does occur *via* the alkene, but that the reaction of the alkene with deuterium ion, with persulfate, or with carbonium ion to initiate polymerization are simply competitive reactions. An unequivocal answer to this question would require rate data for individual steps in the reaction scheme. In the absence of these data, we present semiquantitative arguments based on the comparative extents of racemization and deuteration, summarized in Table I.

Although hopes for a dramatic outcome of the H–D exchange reaction were frustrated, the data obtained are of interest. Incorporation of carbon-bound deuterium into the 2-butyl system under conditions similar to the ones employed in this work has been observed by Burwell,[3b] but no information was provided about the exchange location. Recovery of unreacted alcohol and alcohol from hydrolysis of alkylsulfuric acid was effected following Burwell's procedures, and examination by nmr spectroscopy of alcohol isolated from two separate experiments gave results similar to Burwell's. The unreacted alcohol, presumably present in the mixture as oxonium ion, was much less extensively exchanged and racemized than that recovered from ester. The protons most extensively exchanged were those on C-3, the carbon atom adjacent to the carbinol group. In order to exchange at C-2, any given molecule would have to go through the π complex stage at least twice. The small amount of exchange noted at C-1 is surprising.

Possible pathways for the exchanges at C-1 and C-2 in D_2SO_4, beginning at the carbonium ion stage, are shown in the reaction scheme presented in Scheme I.

Scheme I



The reactions outlined ignore the obvious extensions to include deuteration at C-1 and C-4, and the pathway to **6** by way of 2,3-dideuterio-2-butene is not shown.

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[11] G. S. Clark, M.S. Thesis, University of Maine, 1966.

[12] N. C. Deno, W. E. Billups, J. S. Bingman, R. R. Lastomirsky, and R. G. Whalen, *J. Org. Chem.*, **34**, 3207 (1969).

[13] M. J. S. Dewar, *J. Chem. Soc.*, **406** (1946).

[14] (a) R. Taft, *J. Amer. Chem. Soc.*, **74**, 5372 (1952); (b) J. Levy, R. Taft, D. Aron, and L. P. Hammett, *ibid.*, **75**, 1253 (1953); (c) E. Purlee and R. Taft, *ibid.*, **78**, 5807 (1956); (d) P. Riesz, R. Taft, and R. Boyd, *ibid.*, **79**, 3724 (1957); (e) R. Boyd, R. Taft, A. Wolf, and D. Christman, *ibid.*, **82**, 4729 (1960).

[15] A. Shilov, R. Sabirova, and V. Gorshkov, *Dokl. Akad. Nauk SSSR*, **119**, 555 (1958); *Chem. Abstr.*, **53**, 6988 (1959).

Loss of proton is not considered reversible because of the low concentration of proton available. The deuterations of alkene are marked as questionable because it is this possibility that we are discussing. The notation "π complex (H^+)" means a species with a protonated, as opposed to deuterated, double bond.

All of the cations, $C_4H_9^+$ and **1**–**6**, may revert to ester or alcohol, and be recovered as "free" alcohol or as alcohol from hydrolysis of the ester. As mentioned earlier, there is very little alcohol present that has not been through one or more steps of this sequence, for a total of about 90% of the recovered alcohol is racemic.

Examination of Table I shows that of the "free" alcohol recovered in runs D-1 and D-2, an average of 23% has been deuterated at C-2, and therefore must have reached one or more of the stages **3**, **4**, and **5** if π complexes represent the major pathway for deuteration. The same table shows that an average of 96% of the alcohol molecules have undergone exchange at C-3. If 23% also is substituted at C-2, some must be doubly substituted, at the very least.

Now the degree of racemization of this material is in the range 63–75%, and we see that the number of molecules which have undergone substitution exceeds the number which have been racemized. In other words, *once a molecule reaches the cation stage, it will, on the average, undergo more than one substitution before reverting to alkylsulfuric acid.*

In the case of the alcohol recovered from ester, polydeuteration is the only explanation of the results, which show, on the average, 150% deuteration at C-3 and 58% at C-2. Clearly, some of these species must have arisen from cation **3** and perhaps from **6**.

The point of these arguments is that deuteration is relatively fast, as least as fast as cation formation. If deuteration occurs exclusively or principally by way of alkene, then alkene formation must be rapid. If the persulfate removes only a small part of the alkene, *i.e.*, reduces the steady-state concentration slightly, it cannot be an effective inhibitor, for then polymerization could still occur. However, if essentially all of the alkene is removed, *i.e.*, if its steady-state concentration is reduced by perhaps 90%, then persulfate would be used up rapidly because the alkene is formed rapidly. As we have seen, in 30 min essentially all of the molecules have been at the cation stage, and all have undergone exchange, some more than once. If substitution occurs by way of alkene, then alkene formation also has to be rapid. However, we already have seen that rapid alkene formation should render the small amounts of persulfate ineffective. Our conclusion is that the major pathway to H–D exchange in this system is not through alkene.

The interesting question remains as to the necessity for addition of the persulfate before the alcohol is added to the acid. Why cannot one wait until 15 min after the alcohol and acid are mixed before the first addition? No visible evidence of polymer is present at that time. The answer is that the process of polymerization has begun, even though it is not visible to the eye. One begins to note absorption in the ultraviolet after 4 or 5 min. For samples handled in a comparable manner, transmittances at 307–310 mμ were 0.90, 0.75, and 0.31 (concentrations $\sim 10^{-3}$ M in 96% H_2SO_4, approximately 0°) after 4, 37, and 43 min. Because polymerization, once begun, cannot be halted by the addition of small amounts of persulfate, it is believed that the reaction is autocatalytic.

Hoffman and Schriesheim[16] have suggested that "old" sulfuric acid, previously used as catalyst for butene–isobutene alkylations, and containing cyclopentenyl cations, was responsible for elimination of the inhibition period in that reaction. This investigation showed that neither "old" sulfuric acid, previously used in a polymerization reaction, nor solutions of cyclopentenyl cations prepared by dissolving alkylated cyclopentadienes in concentrated sulfuric acid had any noticeable influence on the rate at which polymer formed in our systems. When the supposed catalysts were used in the absence of $K_2S_2O_8$, the maximum formation of ester occurred at the same time as in the absence of the additives. When "old" acid or acid containing cyclopentenyl cations was added to systems stabilized by $K_2S_2O_8$, no polymerization occurred.

We propose that the acid-insoluble polymer is responsible for the autocatalytic nature of the polymerization process, and the characteristic responsible for its catalytic activity is its high degree of unsaturation.[7] Addition of some of the acid-insoluble polymer, prepared in a previous run, was shown to catalyze further polymerization, and to render ineffective the persulfate being added to the system. When the polymer was fractionated, it was found that only the higher boiling fractions, which were also highly unsaturated, were effective in promoting polymerization.

We believe that the reason the persulfate is unable to attack the alkene linkages in the polymer effectively is that the polymer is present in a separate organic phase even when present in trace amounts, and perhaps because the alkene linkage is sterically protected by branching methyl groups nearby. The persulfate is soluble only in the acid layer. Although persulfate is unable to attack the higher molecular weight alkenes, carbonium ions are able to do so by virtue of their being largely organic. They, together with the polymer, may form a micelle-like aggregate with the localized charge of the cation presented to the acid phase. The unsaturated linkages are protected within the polymer phase, but the cations may migrate along or within the micelle until they find suitable sites for reaction. The subsequent reactions may then include the hydride transfers, rearrangements, C–C chain splittings, deprotonations, cyclizations, etc., which result in the large number of relatively stable products.

Experiments with other alcohols showed that 2-pentanol was similar to 2-butanol, except that larger amounts of potassium persulfate were required to prevent polymerization. Several experiments with cyclohexanol indicated that persulfate could stabilize it against polymerization, although the alcohol did not show the same tendency as 2-butanol or 2-pentanol to polymerize. 2-Octanol did not polymerize within 2 hr in 96% H_2SO_4 at 0°, and the esterification curves with and without $K_2S_2O_8$ were superimposable. When the mole ratio of acid to alcohol was increased to 10:1, 2-octanol and 2-butanol polymerized even in the presence of $K_2S_2O_8$.

Experiments with 2-butene, an equimolar amount of water, and 98% sulfuric acid in the presence of $K_2S_2O_8$

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(16) J. Hoffman and A. Schriesheim, *J. Amer. Chem. Soc.*, **84**, 958 (1962).

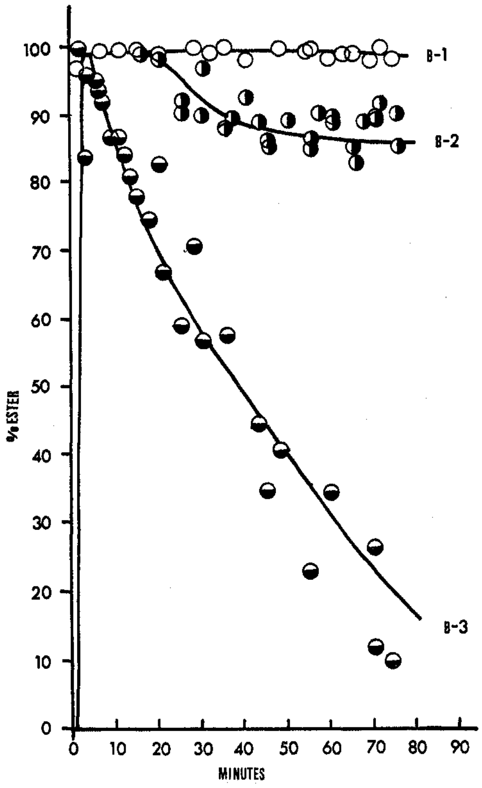

Figure 3.—Esterification of 2-butene with sulfuric acid: B-1, no $K_2S_2O_8$, −40°; B-2, with $K_2S_2O_8$, mixed and kept at −40° for 5 min, warmed to 0°; B-3, no $K_2S_2O_8$, mixed at −30°, warmed to 0°. The mole ratio acid/alcohol was 5.0 for all runs. Maximum per cent ester was normalized to 100 for all runs.

support our conclusions regarding the action of persulfate. Small amounts (1 mol % based on 2-butanol) of 2-butene introduced into a stabilized system of sulfuric acid–2-butanol at 15 min after starting the run did not cause polymerization, but large amounts of 2-butene mixed with H_2SO_4 and water polymerized despite the presence of $K_2S_2O_8$ unless special precautions were observed.

If 1 mol of butene was added to 5 mol of 96–98% sulfuric acid containing an additional 1 mol of water, at −40 to −60°, and if the temperature was kept very low, no inhibitor appeared to be necessary. If the mixture was allowed to warm up to 0°, polymerization occurred as with the alcohol. If the solution was prepared in the presence of $K_2S_2O_8$ but the initial temperature and rate of addition were adjusted so that the temperature quickly reached 0° after addition of the butene, polymerization occurred. On the other hand, if the mixture was allowed to stay at the low temperature for at least 5 min before warming to 0°, the persulfate was able to protect against polymerization. Evidently a little time is required for complete conversion of all of the butene to alkylsulfuric acid. Figure 3 shows the results of several experiments. Note that in curve B-2, the concentration of alkylsulfuric acid appears to be levelling off at between 80 and 90%, which is the concentration reached by stabilized mixtures of 2-butanol and sulfuric acid after several hours.

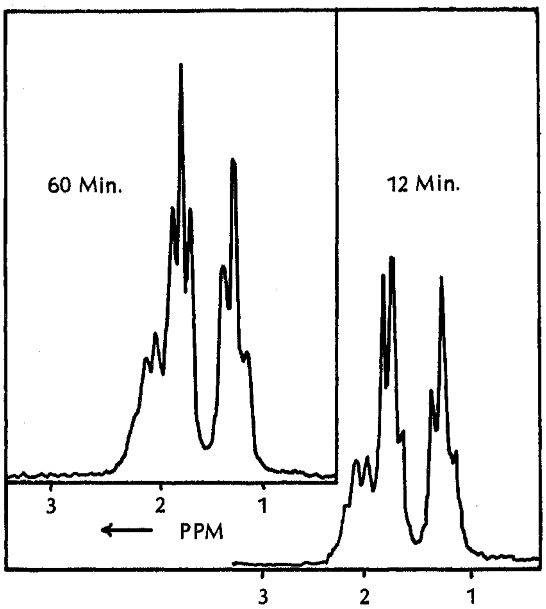

Figure 4.—Portions of nmr spectra of 2-butanol–H_2SO_4–$K_2S_2O_8$ after 12 and 60 min, showing conversion of ROH_2^+ to $ROSO_3H$.

The nmr spectrum of such a system after 15 min was similar to that of a mixture of 2-butanol–sulfuric acid–$K_2S_2O_8$ after 90 min, and remained unchanged for at least 1.5 hr when stabilized with $K_2S_2O_8$ in the same manner as in the experiments with 2-butanol. An interesting point which appears not to have been reported in the literature may be seen in the nmr spectra of stabilized solutions of 2-butanol after 12 and 60 min reaction time (Figure 4). The "triplet" centered at 1.76 ppm may be noticed to vary considerably with time. We interpret these peaks as due to the protons on C-1 of the oxonium ion of 2-butanol and of *sec*-butylsulfuric acid. Reading from the left, the first peak is due to alkylsulfuric acid. The middle peak is a combination of alkylsulfuric acid and alkoxonium ion. The third is due to alkoxonium ion. As the reaction proceeds, the intensity of signal due to the alkylsulfuric acid increases while that due to alkoxonium ion decreases. The same result may be observed in the two smaller peaks that are visible at just over 2 ppm. The right-hand peak increases with time. As might be expected, the oxonium ion deshields adjacent protons somewhat more effectively than does the sulfuric ester.

Experimental Section

Sulfuric Acid and Deuterium Sulfate.—Analyzed reagent grade H_2SO_4 was stored in a container that could be pressurized with dry air and that was fitted with a wash-bottle type adapter with a Teflon stopcock attached to the outlet. Deuterium sulfate was prepared by addition of 99.8 mol % D_2O to SO_3, following a modification of a method of Herber.[17] The product was 97.8% D_2SO_4 by weight; its isotopic purity, by nmr spectral analysis, was 99.8 mol %.

2-Butanol and Other Alcohols.—2-Butanol from various sources rapidly produced a yellow color when a few drops were mixed with concentrated sulfuric acid. Infrared examination showed the presence of a small absorption band, presumably due to the carbonyl group, at 1715 cm^{-1}. Purification was accomplished by washing the 2-butanol three times with aqueous $NH_2OH \cdot HCl$, then distilling the desired product away from the oximes and excess reagent under reduced pressure (pot temperature below 50°). The distillate was then dried (K_2CO_3) and redistilled through a 50-plate column, bp 99–100°. No evidence could be found for the presence of a carbonyl group, and a sharp hydroxyl proton doublet in the nmr spectrum at δ 5.1 ppm (neat) showed that the alcohol was dry.

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[17] R. H. Herber, *Inorg. Syn.*, 7, 155 (1963).

2-Pentanol and other alcohols were purified by standard procedures. All were examined by ir and nmr, and subjected to the color test with sulfuric acid.

(+)-2-Butanol.—α-Pinene, $[\alpha]^{25}\text{D}$ +47.40, was prepared from β-pinene[18] by the method of Richter and Wolff.[19] Brown's method[20] was used to convert *cis*-2-butene to the optically active alcohol. On our hands, the product instantly developed a brilliant orange-yellow color in contact with sulfuric acid, and showed a strong carbonyl peak in its infrared spectrum at 1670 cm^{-1}. Careful distillations improved the alcohol only slightly, so it was subjected to the purification described above. Optical rotation varied somewhat from batch to batch; the highest value was $[\alpha]^{25}\text{D}$ +10.40.

Apparatus.—The reaction vessel was a 500-ml four-neck flask, equipped with a ground stirrer shaft and bushing in the center neck. Other necks were adapted for a low-temperature thermometer, for admission of nitrogen gas when desired, and for a serum cap through which gas samples could be withdrawn with a syringe. One neck either supported a buret modified for rapid addition of the alcohol or was used for the periodic addition of $K_2S_2O_8$ and removal of samples for titration.

The stirrer and flask were both mounted on the same swiveling vertical support rod, making it possible to raise the flask quickly from a solid CO_2–ethanol bath, rotate it by 180°, and immerse it in a well-stirred ice–water bath. The stirrer blade for the reaction mixture was a modified Hershberg type made of tantalum wire.

Esterification of 2-Butanol with Sulfuric Acid.—A weighed amount of H_2SO_4 or D_2SO_4 was placed in the reactor, the stirrer was started (positive nitrogen pressure), and the acid was cooled to −20 to −30°. The acid often froze upon cooling, but this did not offer much of a problem if the stirrer was kept running.

The required amount of 2-butanol was then added as quickly as possible from a pressurized buret. Usually, the addition required 40–50 sec, and the temperature of the system would be just under 0° when addition was complete. The timer was started at this point, and the reactor was immersed in the 0° bath.

If $K_2S_2O_8$ was used as a polymerization inhibitor in a run, a portion equivalent to 0.25 mol % of the alcohol to be used was added just prior to addition of the alcohol, and like portions were added each 15 min thereafter, or as desired in special experiments. Other additives, such as methylcyclopentane, were used as desired.

Samples of the reaction mixture, about 2.0 g each, were periodically withdrawn from the flask, using a succession of cleaned and dried pipets each topped with a 2-ml dropper bulb, and quickly transferred into half-pint tared vacuum bottle fillers[21] containing about 30 g of ice. Sample weights were obtained by difference.

At the end of a run, each individual sample was titrated with standardized 1.0 *N* NaOH solution delivered from a weighing buret. The quenched samples showed no change in titratable acid over a period of several hours.

Esterification of 2-Butene with H_2SO_4.—Sulfuric acid was placed in the reactor and cooled as in the experiments with 2-butanol, and butene was allowed to run in from a trap in which an approximately weighed amount had been collected. The delivery tube was arranged so that the butene ran directly onto the surface of the frozen H_2SO_4–air emulsion. The addition time in all successful runs was between 45 and 60 sec. It appeared that avoidance of local heating and keeping the overall temperature below −20 or −25° was necessary to avoid polymerization. In some runs, the temperature was raised to 0° as quickly as possible. In the runs that were successfully stabilized against polymerization, the mixture was held at a low temperature (−40°) for at least 5 min before warming it to 0°. Samples of gases taken from over the mixture in the reaction flask and subjected to gas chromatographic examination after that period of time showed no traces of butene.

Samples of the mixture were then obtained and titrated as in the experiments with the 2-butanol.

Evolution of Gases from the 2-Butanol–H_2SO_4 System at 0°.—Runs were prepared as for the esterification experiments, except that no nitrogen flowed through the reaction flask. The vapor phase over the system was periodically sampled by removal of 5 ml of gas in a syringe and analysis by gas chromatography on a silica gel column. The same method was used for sampling for butene, isobutane, or *n*-butane in the experiments with hydride donors. The amount of gas found in the sample was converted to moles present in the vapor space over the sulfuric acid by application of a factor calculated using the volume of vapor space in the reaction flask, temperature, volume of sample, and the ideal gas laws. The method was calibrated using known mixtures.

Ultraviolet Spectra in H_2SO_4.—From mixtures of 2-butanol or 2-butene and sulfuric acid prepared as for esterification runs, either with or without $K_2S_2O_8$, samples were removed and diluted with cold concentrated sulfuric acid to approximately 2.5×10^{-3} *M* concentration of alcohol and the spectra were recorded immediately on a Perkin-Elmer Model 4000 Spectracord.

Nuclear Magnetic Resonance Spectra of 2-Butanol and Related Products in H_2SO_4.—Nmr spectra were recorded on a Varian A-60 instrument with tetramethylsilane sealed in a capillary tube as an external standard. Spectra in H_2SO_4 and D_2SO_4 were run at 0°.

Registry No.—Potassium persulfate, 7727-21-1; 2-butanol, 78-92-9; sulfuric acid, 7664-93-9; *n*-butane, 106-97-8; 2-butene, 107-01-7.

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[18] We thank Dr. H. I. Enos, Jr., Pine and Paper Chemicals Research Division, Hercules Powder Company, Wilmington, Del., for a gift of optically active α- and β-pinenes.

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[21] Filler No. 01B, Aladdin Industries, Inc., 705 Murfreesboro Road, Nashville, Tenn.