TABLE III

ALKOXY ACIDS AND THEIR ESTERS[a]

Compound	B. p. °C.	Mm.	n^{25}_{D}	d^{25}_{4}	Mol. refraction Calcd.	Found	Neut. equiv. Calcd.	Found
$CH_3OCH_2CH_2COOH$	102	13	1.4160	1.0982	23.85	23.76	104	106
$C_2H_5OCH_2CH_2COOH$	108	10	1.4178	1.0450	28.47	28.44	118	118
n-$C_3H_7OCH_2CH_2COOH$	76	1	1.4204	1.0043	33.09	33.29	132	133
i-$C_3H_7OCH_2CH_2COOH$	70	1	1.4222	1.0032	33.09	33.43	132	131
n-$C_4H_9OCH_2CH_2COOH$	72	0.1	1.4240	0.9876	37.71	37.73	146	146
$CH_3OCH_2CH_2COOCH_3$	63	40	1.3993	1.0052	28.59	28.40	118[b]	119[b]
$C_2H_5OCH_2CH_2COOC_2H_5$	60	13	1.4041	0.9461	37.82	37.77	146[b]	145[b]
n-$C_3H_7OCH_2CH_2COOC_3H_7$-*n*	87	13	1.4139	0.9369	47.06	46.40	174[b]	170[b]
i-$C_3H_7OCH_2CH_2COOC_3H_7$-*i*	67	13	1.4059	0.9150	47.06	46.71	174[b]	170[b]
n-$C_4H_9OCH_2CH_2COO.C_4H_9$-*n*	97	6	1.4190	0.9109	56.30	56.00	202[b]	198[b]

[a] Data for hydracrylates in Table I. [b] Saponification equivalents.

Methyl β-(β-Methoxypropionoxy)-propionate.—Combined distillation residues (77 g.) from acid catalyzed experiments with methanol were distilled through a short column. Only one fraction could be collected before pyrolysis set in. This fraction was methyl β-(β-methoxypropionoxy)-propionate; b. p. 86° (1.5 mm.), wt. 29.4 g., n^{25}_{D} 1.4260.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.51; H, 7.37; mol. wt., 190; sapn. equiv., 95. Found: C, 50.58; H, 7.37; mol. wt. (ebullioscopic in benzene), 187; sapn. equiv., 94.

Summary

The base catalyzed reaction of β-propiolactone with alcohol is rapid and results in hydracrylates. Without added catalysts, alkoxy acids are slowly formed. The acid catalyzed reaction gives alkoxy acids by direct reaction and hydracrylates by alcoholysis of poly-ester acids formed in the competing polymerization of the lactone. The effects of time, temperature and catalyst concentration on the proportions of products in the mixture are demonstrated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Evidence of an Induction Period in the Alkylation of Isobutane by 2-Butene

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The reaction between isobutane and 2-butene at 0° in the presence of 96% sulfuric acid is not extremely rapid. This may be shown by passing 2-butene gas at a constant rate into a stirred mixture of sulfuric acid and isobutane. In our experiments the isobutane was initially at atmospheric pressure; the isobutane consumption was measured by observing the input of isobutane required to maintain a constant pressure in the reactor. Figure 1 shows the observations made during a typical experiment.

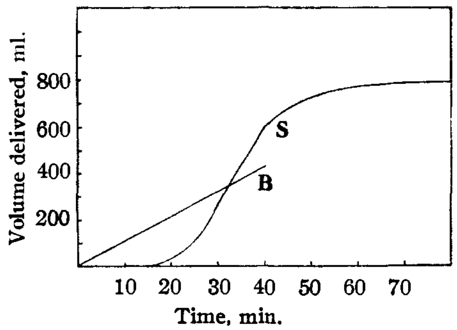

Fig. 1.—Rate of consumption of isobutane (S) gas produced by the addition of 2-butene (B) gas at a constant rate, in sulfuric acid.

At first little or no isobutane is consumed. After about twenty minutes, during which about 200 ml. of 2-butene has been introduced, the consumption of isobutane approaches a constant rate. When the 2-butene supply is shut off the consumption of isobutane continues for over an hour. These periods will be referred to as the induction period, the steady state period and the terminal reaction period, respectively. When the steady state is established the rate of consumption of isobutane is two to three times that of 2-butene. The best yields of alkylate accompanied the higher ratios. An approximate calculation shows that if the alkylation reaction involves a ratio of unity and if the condensed isoöctanes dissolve the expected amount of isobutane, a ratio of about three should be observed. Any ratio less than that involves polymerization or other consumption of 2-butene apart from alkylation.

The reaction studied is a complex one leading to a variety of products.[1a,b,c] Under the conditions

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[1] (a) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941), list two main fractions of trimethylpentanes and some 2,3-dimethylbutane from the reaction catalyzed by sulfuric acid. (b) L. Schmerling, THIS JOURNAL, **68**, 275 (1946), lists nineteen products from the reaction catalyzed by aluminum chloride. (c) M. H. Gorin, C. S. Kuhn and C. B. Miles, *Ind. Eng. Chem.*, **38**, 795 (1946), list six fractions from the reaction catalyzed by hydrogen fluoride.

described here, a poor yield of liquid alkylate is obtained prior to establishment of the steady state; but if a liter or more of the alkene is used up, and the reaction is allowed to run to saturation with the isobutane, a good yield (5–6 ml. per liter of gaseous alkene) of alkylate can be obtained. About half of the alkylate distils above the isoöctane range. For present purposes the initial predominating net reaction will be considered to be

$$C_4H_8(\text{gas}) + C_4H_{10}(\text{gas}) \xrightarrow{H_2SO_4} C_8H_{18}\ (\text{liquid and dissolved } C_4H_{10})$$

and attention centered upon the factors which start the series of events leading to the formation of the actual products.

The Rate of Solution of 2-Butene.—It was necessary to know the instantaneous partial pressure of 2-butene in the reactor during introduction of the gas. This was observed with the reactor filled with nitrogen gas. As the flow of 2-butene was started the pressure in the reactor rose from five to twenty mm., depending upon the rate of flow of the 2-butene. A rise of 1 mm. of pressure corresponded to about 1 ml. of gas. This increase in pressure does not represent merely an accumulation of 2-butene as gas in the reactor, however, since whenever the flow of 2-butene was stopped the decrease in pressure was only 1–3 mm., and was complete in about one minute. Part of the permanent pressure increase, after starting and stopping the 2-butene, was eventually shown to be mechanical, *i. e.*, some 2-butene lodged in the manometer line. The remainder was due to an actual evolution of isobutane, produced through dismutation of the alkene, and will be dealt with separately. A pressure increase would operate to delay an apparent consumption of isobutane during alkylation, since isobutane entered the system only as a result of pressure drop. However, delay from this cause was a minor effect, inasmuch as the isobutane consumption eventually reached 20–30 ml. per minute; the observed induction is therefore extended by not more than one minute by this gas accumulation. Neither is the apparent induction due to slowness in the rate of solution of the 2-butene.

The Steady State Concentrations.—The delay in apparent isobutane consumption could have been due merely to a low specific reaction rate, in which case a finite concentration of 2-butene in the system would have to be built up before a steady-state condition would be reached. Experiments were accordingly made in which a part of the 2-butene was introduced rapidly, followed by a waiting period, with finally the usual slow addition of the alkene at a constant rate. Such a course is plotted in Fig. 2. It is seen that the isobutane consumptions of Figs. 1 and 2 are similar; the rate of reaction is not dependent merely upon the amount of 2-butene present but involves the production of a steady-state concentration of some intermediate compound.[2] The type of experiment shown in Fig. 2, which arrived at a given steady-state condition through a variation in the time of input of a critical amount of reactant, was performed many times and never failed to show a period of induction.

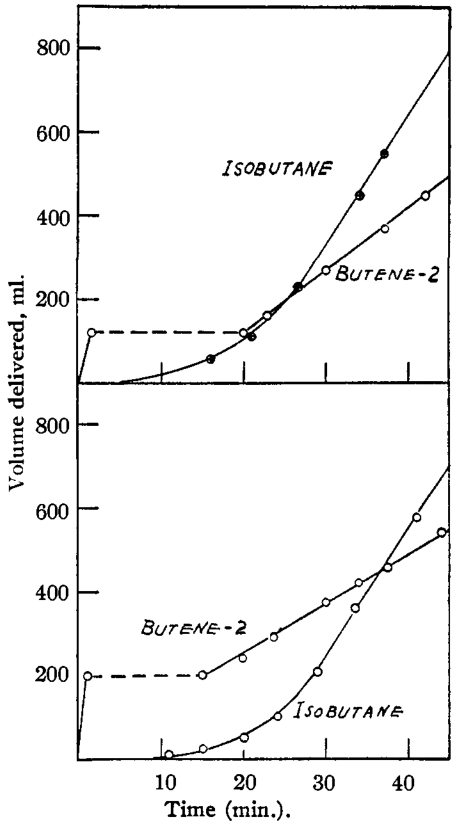

Fig. 2.—Rate of consumption of isobutane gas with interrupted addition of 2-butene.

Factors Affecting the Induction Period.—The length of the induction period may be varied by changing the rate of introduction of 2-butene and the amount of sulfuric acid present in the reactor. Table I presents some typical data.

TABLE I

INDUCTION PERIOD AS A FUNCTION OF RATE OF BUTENE INPUT

Volume acid, ml.	Rate of butene-2 input, ml./min.	Induction period, min.
25	7.5	35
25	7.5	32
25	10	25
25	13	18
25	24	18
25	30	15
100	10	40
100	12	38
100	30	22

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(2) We see no evidence for the assumption that removal of inhibitors is responsible for the induction period.

It is seen that with increasing rate of input with either 25 ml. or 100 ml. of catalyst present, the induction time is decreased; a three-fold increase in rate of alkene input about halves the induction period. The four-fold increase in acid at a given rate of input less than doubles the induction period. It is evident that isobutane consumption is not related to a concentration of accumulated 2-butene as such; at the lower rates of input the time available for production of the critical intermediates tends to shorten (relatively) the induction period. Both a time and a concentration factor are required for the production of the steady-state condition.

The addition of about 0.005 mole of secondary butyl alcohol shortened the induction period from twenty-five minutes to seventeen minutes, but a similar amount of *t*-butyl alcohol more than halved the induction period (Fig. 3). The reaction of isobutylene with isobutane passes through a similarly shortened induction period.

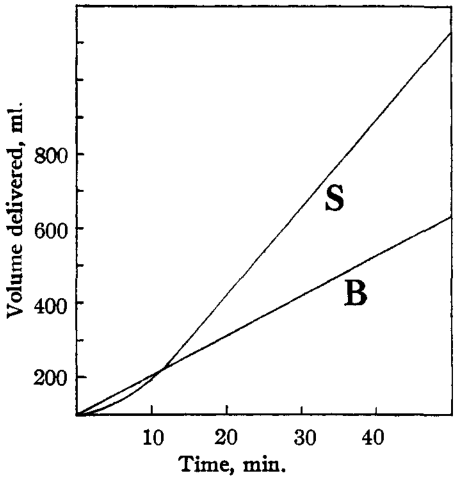

Fig. 3.—The effect upon the induction period of added *t*-butyl alcohol: S, isobutane; B, butene-2.

The presence of liquid alkylate made no difference in the length of the induction period. This was shown in two ways. A sample of the alkylate was recovered by steam distillation from the diluted contents of the reactor; after drying, this sample was added to fresh sulfuric acid in the reactor, with the same result as in the absence of the alkylate. In other cases the 2-butene was shut off, and saturation of the system with isobutane was started. In varying times after cessation of the flow of the alkene, a new run was started. The length of the new induction period depended upon the time of saturation. After two hours the used catalyst behaved as fresh catalyst and the induction period was normal; after one hour of saturation the induction period was about half of normal (see Table II). After twenty minutes the consumption of isobutane was slow but readmission of 2-butene was accompanied by only a short induction period.

Table II

Comparison of the Induction Periods in Fresh and Used Catalyst; the Effect of Saturation Time

Rate of butene input, ml./min.	Time of saturation, min.	Induction period Used acid	Induction period Fresh acid
5	19	10	Long
7.5	35	15	32
10	42	15	25
8	50	16	30
16	100	16	18
11	120	18-20	20

Apparently a long-lived intermediate reacts with isobutane and also promotes establishment of the steady state condition.

The induction period was not affected by the partial pressure of the isobutane. In one experiment, using 25 ml. of sulfuric acid, the reactor was filled with equal partial pressures of nitrogen and isobutane, and the 2-butene introduced at 10 ml./min. The induction period was twenty-five minutes. In this case the ratio of isobutane to 2-butene during the steady state was about 1.5, since, at the reduced partial pressure of the isobutane, less of the alkane dissolved in the alkylate.

Discussion of Results.—A mechanism of the type suggested by Schmerling[1b] lends itself to an explanation of an induction period in the reaction studied. The essential feature of this mechanism is based upon the fact that isobutane acts as a reducing agent upon certain carbinol derivatives in the presence of alkylation catalysts.[3] In so doing it is oxidized to the *t*-butyl derivative.

$$(CH_3)_3CH + R'X \xrightarrow{\text{catalyst}} (CH_3)_3CX + R'H$$

The latter reacts with the alkene component of the alkylation, under the influence of the catalyst, to produce RX, which is reduced by isobutane either before or after isomerization to a form R'X.

$$C_nH_{2n} + (CH_3)_3CX \longrightarrow RX \text{ and } R'X \xrightarrow{\text{iso-}C_4H_{10}} RH \text{ and } R'H + (CH_3)_3CX$$

The intermediates RX and R'X may be considered as solvated carbonium ions, R^+ and R'^+ as outlined by Bartlett and co-workers.[3] The multiplicity of products is accounted for by side reactions and by the multiplicity of possible rearrangement products and their specific reaction rates toward isobutane, 2-butene and cracking. The reaction of isobutane, however, rests upon the above transhydrogenation with these intermediates, the concentrations of which are initially zero and reach a steady state value as 2-butene is introduced. The rate-determining step[4] in the

(3) See also Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945); Paul D. Bartlett, Francis E. Condon and Abraham Schneider, This Journal, **66**, 1531 (1944); L. Schmerling, *ibid.*, **66**, 1422 (1944).

(4) An editorial referee points out that the main reactions occurring during the induction period are of the type classified by Ipatieff and Pines (*J. Org. Chem.*, **1**, 464 (1936)) as conjunct polymerization. This is polymerization accompanied by *trans*-hydrogenation and results in saturated and unsaturated hydrocarbons; the latter are considered to undergo transhydrogenation with isobutane; the

formation of the final products could be a reaction rearrangement. The time required to approach steady-state conditions is largely independent of the activity of the isobutane, but is influenced by the rate of input of 2-butene, by the stirring and by the amount of catalyst. The steady-state concentration of a *t*-butyl derivative can be approached by adding *t*-butyl alcohol or isobutylene; otherwise it is built up by isomerization of the normal butene or through transhydrogenation reactions involving polymers of 2-butene and isobutane.

Further evidence pointing toward the viewpoint outlined above is observed in a study of the kinetics of the terminal reaction which will be reported separately.

Apparatus and Materials.—The reactor vessel was a 500-ml. three-necked flask fitted with a separatory funnel and a Hershberg-type stirrer made of nichrome wire. The stirrer shaft was housed in a vacuum and pressure tight bearing; the stirrer was of such size that it was not completely covered by 25 ml. of sulfuric acid but was completely covered by 100 ml. of acid. At the bottom of the flask a glass capillary tube, which carried a stopcock, was sealed in. The reactor could be filled, emptied, and washed without disturbing any of the connections; it was surrounded by a metal tub which held cracked ice and water. The degree of agitation could be varied; normally there was violent spattering of the liquid phase.

Into an opening of the reactor was passed one arm of a T-tube; a second arm was connected to a mercury manometer, while the third arm was used to lead in the desired gases. The isobutane and 2-butene were stored over 85% phosphoric acid under a hydrostatic head held constant automatically. The 2-butene line contained a pump designed to deliver gas at small, constant, rates of flow even against minor changes in pressure; the pump was bypassed by a line used for rapid delivery of 2-butene. The flow of isobutane was controlled by an automatic gas valve which was actuated by a mercury manometer connected to the line of the main manometer. The gas pressure in the isobutane gasometer was always constant and essentially the same as the total pressure in the reactor, since rates of flow were low.

A typical procedure involved testing for leaks under both vacuum and pressure; evacuation of the reactor to less than 1 cm. pressure; delivery of the desired amount of 96% sulfuric acid to the cooled reactor; flushing out and filling the reactor with isobutane gas; stirring to assure saturation of the sulfuric acid and adjusting the pressure; starting the 2-butene pump and thereafter recording the delivered volume of the two gases.

The sulfuric acid used was Baker and Adamson C.P. 96% acid. The 2-butene and isobutane were of highest purity, supplied by the Shell Development Co., Emeryville, California. Several different batches, of better than 99% purity, gave the same results.

Acknowledgment.—We wish to acknowledge the assistance of the Shell Development Co. in furnishing the pure isobutane and 2-butene for this investigation. We are also indebted to Miss Eva Herzberg, of this Laboratory, whose preliminary work suggested the existence of an induction period in the reaction studied.

Summary

Gaseous 2-butene was passed at a constant slow rate into a vessel filled with isobutane and containing vigorously stirred 96% sulfuric acid at 0°. The 2-butene dissolved rapidly without reaction of the isobutane; after from ten to twenty-five minutes, consumption of isobutane started and from then on the ratio of the two gases consumed was constant. The length of the induction period was largely independent of the time required to introduce a given amount of 2-butene, and was not affected by the presence or absence of an oil phase initially. It was affected by the rate of continued addition of the alkene, by the amount of acid present, and by the addition of small amounts of *t*-butyl alcohol. It is concluded that steady state concentrations of intermediate compounds develop during an inhibition period, consisting of (1) *t*-butyl derivatives, which react with the incoming 2-butene, and (2) the products of that condensation, which undergo transhydrogenation with isobutane, in accordance with Schmerling's mechanism.

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former conceivably dealkylate and the resulting alkene portions also engage in transhydrogenation. The initial rate of reaction of isobutane, he considers, "may be dependent on the actual concentration of olefinic polymer present, and the rate of transhydrogenation of isobutene with the polymers of 2-butene and also the rate of the dealkylation reaction." These factors would be influenced by the experimental conditions and "would not require the assumption of long-lived intermediates of the carbonium type." The point at issue seems to be whether a single course is set for the whole reaction at the start, or whether, after some time, a new course develops which finally predominates. If there is a single path followed from the start, then our induction period is an accident of the experimental conditions, and, we feel, would not be so little influenced by changes in those conditions. But if the Schmerling mechanism operates during our steady state, and is self-perpetuating, then the major, if not only, role of conjunct polymerization is that of a side-reaction which aids in producing a critical intermediate.

The reactions of dealkylation are not observable, nor do they seriously affect the observed rate during the steady state. This is because they are slow compared to the major reaction and are likely to generate as much isobutane as they consume. If the steady-state reaction does not depend largely upon either conjunct polymerization or dealkylation, but rather upon transhydrogenation of products formed from 2-butene and a tertiary butyl derivative present in small amount, there remains in question the identity of the rate-determining step during the steady-state reaction.