

## The Effect of the Solvent on the Catalytic Activity of Potassium *t*-Butylate. The Isomerization of 3-Butenylbenzene

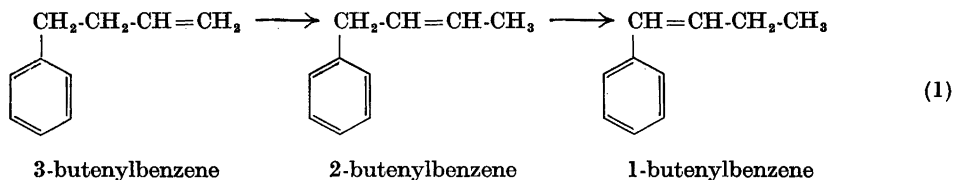
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The isomerization of 3-butenylbenzene to 1-butenylbenzene with potassium-*t*-butylate as catalyst has been investigated kinetically using 1,4-dioxane and dimethyl ethers of ethylene glycols as solvents. The rate of the reaction increases markedly with increasing chain length of the glycol ethers; in hexaethylene glycol dimethyl ether the reaction rate is 135 times higher than that in monoethylene glycol dimethyl ether, at constant conditions of 60°C and 0.100 M catalyst concentration. In 1,4-dioxane at the same conditions the rate is only 1/2000 of that in hexaethylene glycol dimethyl ether. The rate will depend mainly upon the capacity of the solvent to solvate the alkali ion specifically. In the polyethylene glycol dimethyl ethers several oxygen atoms in the same molecule cooperate in the solvation of the K<sup>+</sup> ion.

In a recent paper<sup>1</sup> dealing with the conjugation isomerization of unsaturated fatty acid esters in diethyl ether solution with potassium *t*-butylate as catalyst the authors showed that small additions of the dimethyl ethers of polyethylene glycols greatly increased the rate of the isomerization. The effect of the ethylene glycol dimethyl ethers increased with increasing chain length of the ether. However, due to the high rate of reaction caused by small amounts of the most active ethers the investigation of this solvent effect was restricted to small concentrations of the different ethylene glycol dimethyl ethers. In order to compare the solvent effect of the ethylene glycol dimethyl ethers in pure form, the isomerization of 3-butenylbenzene with potassium *t*-butylate as catalyst has been investigated.

The isomerization of 3-butenylbenzene takes place in two steps as follows:



of which the first step is rate determining.

As discussed later, this is made probable in our case by the high rate of isomerization of allylbenzene.

## EXPERIMENTAL

### Procedure

Dry potassium *t*-butylate was dissolved in various solvents to give the desired concentrations. The isomerization reaction was usually carried out in 20 ml test tubes fitted with glass stoppers. 5 ml of freshly prepared catalyst solution was pipetted into the test tube and the temperature adjusted to 60°C in a constant temperature glycerol bath. At time zero a micro beaker containing 100 mg of 3-butenylbenzene was dropped into the catalyst solution and the test tube was shaken vigorously. After a given time the reaction was stopped by addition of methanol. The whole procedure, including the preparation of the catalyst solution, the transfer of the micro beaker and the isomerization reaction, was carried out in an atmosphere of nitrogen.

The isomerization of allylbenzene in dioxane solution at 25°C was carried out in the same way. Because of the long reaction times required for the isomerization of 3-butenylbenzene in dioxane solution at 60°C, the reactions were in this case carried out in sealed ampules.

The reaction product 1-butenylbenzene has the double bond in its chain conjugated with the benzene ring, causing a strong absorption in the U.V. spectrum. The degree of isomerization was followed with a Beckmann spectrophotometer model DU. The wavelength for maximum absorption was found to be at 250 mμ for 1-butenylbenzene and at 249 mμ for 1-propenylbenzene.

### Reagents

*3-Butenylbenzene.* 120 g of sodium wire was put into 1200 ml absolute ether. 285 ml benzylchloride (Fluka A.G. *purum* quality, 99 %) and 215 ml allylbromide (Fluka A.G. *purum* quality, 95 %) was added and the mixture was left at room temperature. After one week another 120 g of sodium wire was added. After three weeks 100 ml of allylbromide was added and another 120 g of sodium. More sodium was added every fortnight until the surface of the added metal remained bright. The liquid was then decanted and washed first with dilute hydrochloride acid, then with water. The ether solution was then dried over Na<sub>2</sub>SO<sub>4</sub>. The ether and some of the diallyl formed were removed by distillation at atmospheric pressure until the temperature of the boiling liquid was 120°C. The remaining liquid was fractionated in a column 25 cm high and 2.5 cm diameter. The column was filled with 3 mm glass beads. The pressure was gradually decreased to 10 mm mercury. The main fraction distilled at 63°C and 10 mm pressure. 26.3 g of 3-butenylbenzene was obtained with  $n_D^{20} = 1.5060$ . A gas chromatogram indicated a pure substance. The literature<sup>3</sup> cites  $n_D^{20} = 1.5059$ .

*Allylbenzene.* Prepared by Theodor Schuchardt GMBH & Co. A gas chromatogram showed a single peak.

*Potassium t-butylate.* The preparation procedure for potassium *t*-butylate in ether solution is given in a recent paper.<sup>1</sup> The ethyl ether solvent was removed under reduced pressure in an atmosphere of nitrogen.

*Ethylene glycol dimethyl ether.* The "purum" quality (99 %) from Fluka A. G. was treated several times with fresh sodium wire until no reaction could be detected on the surface of the metal (usually after one or two weeks). The glycol ether was then distilled in an atmosphere of nitrogen. B.p. 84°C at 1 atm.

*Diethylene glycol dimethyl ether.* The "pract" quality (95 %) from Fluka A. G. was treated with sodium in the way described above, and then fractionally distilled under reduced pressure in an atmosphere of nitrogen.

The same procedure was used to purify the other glycol ethers mentioned below.

*Triethylene glycol dimethyl ether.* The "pract" quality from Fluka A.G.

*Tetraethylene glycol dimethyl ether.* The "purum" quality from Fluka A.G.

*Hexaethylene glycol dimethyl ether* "für der Gaschromatographie" from Theodor Schuchardt GMBH & Co. Unusually much sodium was used.

*1,4-Dioxane* "für Chromatographie" from E. Merck A.G. Treated in the same way as ethylene glycol dimethyl ether. B.p. 100–102°C at 1 atm.

The purity of the above distilled solvents was confirmed by gas chromatograms. Samples taken of the purified solvents showed no base content. The absence of water and alcohol was checked before use by treating samples with potassium.

*Nitrogen.* Fractionated and purified by Norsk Hydro. Nitrogen with argon more than 99.99 %. Water content less than 0.001 %.

*Methanol.* Pro analysi quality from E. Merck A.G.

## RESULTS AND DISCUSSION

In Table 1 are given the results of isomerization of allylbenzene in dioxane solution at 25°C and of the isomerization of 3-butenylbenzene in the same solvent at 60°C. The and value of the extinction coefficient is approximately the same for these two reactions. It may be concluded from the results in Table 1 that the rate of isomerization of allylbenzene at 25°C is about 180 000 times higher than that of 3-butenylbenzene at 60°C.

Bateman and Cunneen<sup>4</sup> isomerized allylbenzene and 2-butenylbenzene in methyl alcoholic alkali at 165°C\* and found only a slight difference in the rate of these two reactions. This verifies the assumption already made that in the isomerization of 3-butenylbenzene it is the first step, the formation of 2-bute-

Table 1. Conjugation isomerization by potassium *t*-butylate (0.100 M) in 1,4-dioxane solution. Molar extinction coefficients after different time intervals for:

a) allylbenzene at 25.0°C.

Time (min)	0.5	1.0	2.0	3.5	5.0	7.5	10.0
Extinction coeff.	4080	7040	11 130	14 450	16 000	16 390	16 900

b) 3-butenylbenzene at 60.0°C.

Time (min)	8520	50 340	110 900	263 520
Extinction coeff.	655	2530	4840	8940

\* In alcohol even these compounds isomerize very slowly because the alcoholate ion is deactivated by H bonds between the alcoholate ion and the alcohol.

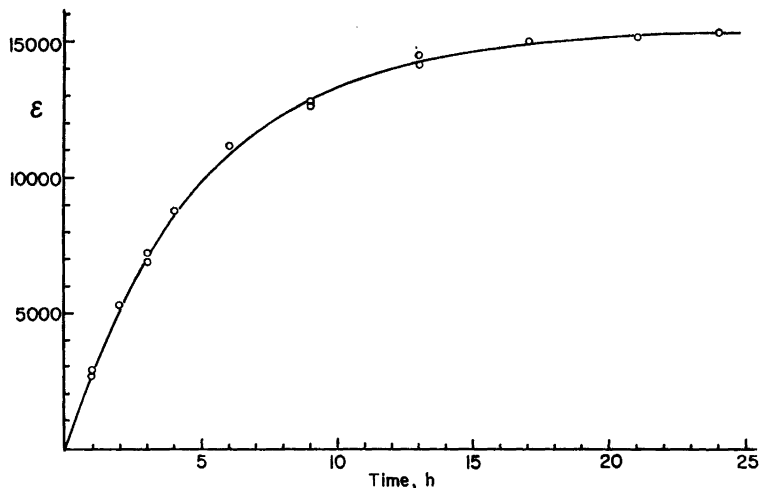


Fig. 1. Isomerization of 3-butenylbenzene by potassium *t*-butylate, 0.100 M in tetraethylene glycol dimethyl ether. Molar extinction coefficient  $\epsilon$  (liter/cm mole) is plotted as a function of the reaction time. Temp. 60.0°C.

nylbenzene, which is rate determining. This is to be expected because the second step involves the removal of a relatively acid H atom from the C atom in the  $\alpha$  position to the benzene ring.

To compare the solvent effects of the various glycol ethers upon the rate of isomerization of 3-butenylbenzene by potassium *t*-butylate, kinetic measurements were carried out in each solvent at 60°C, using 0.100 mole/liter of catalyst.

In Fig. 1 are given the results of measurements made in tetraethylene glycol dimethyl ether. The molar extinction coefficient  $\epsilon$  is plotted against reaction time. Similar plots were obtained in the other solvents. The result in every solvent fitted a first order equation at a constant concentration of catalyst:

$$\ln \frac{\epsilon_E}{\epsilon_E - \epsilon} = (k_f + k_r)t = k't \quad (2)$$

where  $\epsilon$  is the extinction coefficient at the time  $t$ ,  $\epsilon_E$  is the extinction coefficient at equilibrium,  $k_f$  and  $k_r$  are the first order rate constants for the forward and reverse reactions, respectively. The equilibrium is in all cases far over to 1-butenylbenzene so that the experimentally determined constant  $k'$  is approximately equal to  $k_f$ . In each solvent the value of  $\epsilon_E$  was so chosen as to give a constant value for  $k'$ . This value of  $\epsilon_E$  decreased slightly as the solvent changed in the sequence mono-, di-, tri-, tetra-, and hexaethylene glycol dimethyl ether. This difference in the value of  $\epsilon_E$  is possibly due to a different ratio of the *cis-trans* isomers of 1-butenylbenzene. Ultraviolet spectra for *cis* and *trans* isomers of 1-butenylbenzene have not been reported in the literature. For

Table 2. First order rate constant  $k'$  for the isomerization of 3-butenylbenzene in different solvents. Catalyst: Potassium *t*-butylate, 0.100 M. Temperature: 60.0°C.

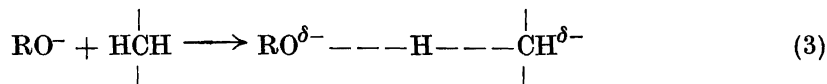
Solvent	$k'$ , hours <sup>-1</sup>	Relative rates
1,4-Dioxane		0.06
Ethylene glycol dimethyl ether	0.00313	1
Diethylene glycol dimethyl ether	0.0339	11
Triethylene glycol dimethyl ether	0.102	33
Tetraethylene glycol dimethyl ether	0.203	65
Hexaethylene glycol dimethyl ether	0.421	135

1-propenylbenzene the maxima are:<sup>5</sup> *cis*: 13 800 at 240.6  $m\mu$ ; *trans*: 17 300 at 249  $m\mu$ . For 1-butenylbenzene we may expect figures close to these.

In Table 2 are given the values of  $k'$  and the relative rates of the reaction in various solvents. As shown, the rate increases markedly with increasing chain length of the solvent up to hexaethylene glycol dimethyl ether. The rate value in 1,4-dioxane is also included in the table for comparison, and is seen to be considerably lower than in ethylene glycol dimethyl ether. The results given in Table 2 indicate that for the potassium *tert*-butoxide catalyzed isomerization of olefins the polyethylene glycol dimethyl ethers of high chain length may be as effective a reaction medium as dimethyl sulfoxide.<sup>19</sup>

In aprotic solvents the potassium *t*-butylate probably exists partly as ion pairs or larger ion aggregates and it is not possible to say *a priori* what are the catalysing entities.

The formation of the transition state leads to a dispersion of the negative charge:



where  $\text{RO}^-$  is the *t*-butylate. The dispersion of the charge will not be expected to effect the interaction energy with species interacting with the anion at a distance which is relatively large compared to the ionic radius. Therefore, in dilute solution in highly dissociating media, where we have a complete dissociation, we expect to find only small primary salt effects on the rate of the reaction. However, in a less dissociating medium the formation of ion pairs leads to a strong short distance interaction between the anion and the cation. This interaction may be expected to be rather specific, and to differ greatly for the  $\text{RO}^-$  and the transition state anion. Because of the reduction in charge density involved in the formation of the transition state, we may expect that the interaction energy with the alkali ion at short distance will be considerably greater for the  $\text{RO}^-$  ion than for the transition state. In this respect, the formation of ion pairs is similar to the solvating of the anions by hydrogen bonds to protic substances. This also represents a specific short distance interaction which may lead to a great reduction in the rate of the reaction of the anions.<sup>6-10</sup>

Table 3. Isomerization of 3-butenylbenzene with different concentrations  $C_T$  of potassium *t*-butylate. Temperature 60.0°C. First order rate constants  $k'$  calculated from kinetic measurements in:

a) ethylene glycol dimethyl ether

$C_T$ moles/liter	$k'$ hours <sup>-1</sup>	$\frac{k'}{\sqrt{C_T}}$
0.025	0.00160	0.0101
0.100	0.00313	0.0099
0.200	0.00453	0.0101

b) tetraethylene glycol dimethyl ether

$C_T$ moles/liter	$k'$ hours <sup>-1</sup>	$\frac{k'}{\sqrt{C_T}}$
0.025	0.093	0.59
0.050	0.145	0.65
0.100	0.203	0.64
0.200	0.299	0.67

In conclusion we may say that in aprotic solvents the experimental first order rate constant  $k'$  (eqn. (2)) increases when the capacity of the solvent to solvate alkali ions is increased to a point where the potassium *t*-butylate is completely dissociated. In aprotic solvents the catalytic activity of the free *t*-butylate ion is expected to be only slightly dependent upon the solvent.

In Tables 3a and 3b are given the results of rate measurements with different concentrations of catalyst. As shown in the tables, the rate increases approximately proportionally to the square root of the concentration of the catalyst.

The above results indicate that the free  $RO^-$  ions are the only catalyzing species in the present case, although it seems that in both solvents only a small part of the catalyst exists in the dissociated form. Assuming that no aggregates greater than ion pairs are present in the solution, the concentration of  $RO^-$  at a low degree of dissociation is approximately given by

$$C_{RO^-} = \sqrt{K_d \times C_T} \quad (4)$$

where  $K_d$  is the dissociation constant of the ion pair ( $K^+ \bar{O}R \rightleftharpoons K^+ + RO^-$ ) and  $C_T$  is the total catalyst concentration. Assuming the  $RO^-$  ion to be the only catalyzing species, the rate is given by

$$r = k' C_B = k'' C_{RO^-} C_B \quad (5)$$

where  $k''$  is the true second order rate constant (here assumed to be independent of the ionic strength),  $C_B$  is the concentration of 3-butenylbenzene. From eqns. (4) and (5)

$$k' = k'' \sqrt{K_d} \sqrt{C_T} \quad (6)$$

which is in accordance with the results given in Tables 3 a and 3 b. There may be observed a slight decrease in the value of  $k'/\sqrt{C_T}$  (as  $C_T$  decreases) in the case of tetraethylene glycol dimethyl ether, indicating a noticeable degree of dissociation as the concentration of catalyst decreases. It should, however, be noted that in the above treatment it is assumed that the mean activity coefficient of the free ions  $K^+$  and  $RO^-$  does not change noticeably as the value of  $C_T$  varies.

It is generally accepted that the  $K^+$  ion in water is solvated by a primary shell of several relatively strongly bonded water molecules.<sup>11</sup> "Primary solvation" is defined by Bockris as "the number of solvent molecules near to an anion, which have lost their translation degrees of freedom and move as one entity with the ion during its Brownian motion".<sup>12</sup> The primary coordination number of  $K^+$  in water is supposed to be about 3.<sup>11</sup> In other oxygen containing solvents, as dimethyl formamide and dimethyl sulfoxide, such solvation shells are also probable.<sup>13,14</sup> Outside the primary solvation shell there is a secondary shell of solvent molecules. The potential of the ion is not strong enough to keep these molecules bound, but each solvent molecule does attain a mean dipole moment in the direction of the ion. The contribution to the total solvation energy from the secondary solvation shell is supposed to be of considerable importance for alkali ions in water.<sup>15</sup>

We may express the general process of dissociation in the following simplified way:



where the  $K^+$  ion is solvated by a number  $y$  of solvent molecules  $S$ . The concentration of  $RO^-$  and thus the rate of reaction (eqn. (5)) depends on the capacity of the solvent to solvate the  $K^+$  ion. The effect of the polyglycols on the dissociation of potassium *t*-butylate has been ascribed to a cooperation of several oxygen atoms of the same molecule in the solvation of  $K^+$ .<sup>1</sup> It may be concluded from the results given in Table 2 that the  $K^+$  solvating capacity of the glycol ethers increases when the chain length increases up to hexaethylene glycol dimethyl ether, which contains 7 oxygen atoms.

There may be different reasons for this effect: 1) The solvation of the  $K^+$  ion involves a loss in freedom of the solvent molecules. It may be expected that the loss in freedom will be less in the case where the solvating oxygen atoms belong to *one* molecule than where they belong to several smaller molecules. The entropy of the  $K^+$  solvation process with a given number of oxygen atoms should therefore be more favourable in the former case. 2) If the solvation of the alkali ion takes place with several smaller molecules a steric hindrance may occur through the interaction between the different molecules. Thus a greater steric hindrance of the solvation of the alkali ion caused by the interaction of the methyl groups would be expected with two molecules of monoethylene glycol dimethyl ether than with one molecule of triethylene glycol dimethyl ether. A similar steric effect is encountered in the formation of complexes between  $Ni^{++}$  and ethylene diamine and  $N,N'$ -dimethyl ethylene diamine.<sup>2</sup> The association constant for one ligand molecule is only slightly

different in the two cases while the association constant for the second and third ligand molecule is increasingly much smaller in the case of the methyl substituted amine.

Studies on the structure and conformation of the polyethylene glycol chain indicate a *gauche* conformation as the most probable,<sup>16-18</sup> which should be favourable for the formation of structures with co-operation of oxygen atoms from the same molecule in the solvation of the  $K^+$  ion.

There is another factor which may lead to an increase in the dissociating power of the glycol ether with increasing chain length. The number of oxygen atoms from the same chain coordinated around the  $K^+$  ion in the primary shell may be expected to increase when the chain length increases until the maximum coordination number is reached. When only the primary solvation is considered, a further increase in the chain length should not lead to any increase in the dissociating power of the glycol ether. However, a further increase in the effect of the primary solvation may be explained as follows

We assume that a number  $x$  of oxygen atoms from the same molecule participate in the primary solvation shell. If the number of oxygen atoms in the ether molecule is  $n$ , the total number of combinations of  $x$  atoms is given by

$$g = \frac{n!}{x!(n-x)!} \quad (8)$$

This is the number of ways in which one  $K^+$  ion can combine with one ether molecule. Assuming that an ether molecule does combine with only one  $K^+$  ion, and assuming further that all the combinations have the same probability of occurring, this may be expressed as an increase in the entropy of solvation per mole  $K^+$

$$\Delta S = R \ln g \quad (9)$$

This is the entropy increase due to the increase in the number of possible combinations of  $x$  oxygen atoms when the number of oxygen atoms in the ether molecule is increased from  $x$  to  $n$  and the concentration of ether molecules is kept constant. Although not all these combinations can in fact be expected to have the same probability, this consideration may explain at least qualitatively the effect of increasing the chain length of the glycols.

Even if we assume that only  $x$  neighbouring O atoms in the same molecule cooperate in the primary solvation shell we get

$$g = n - x + 1 \quad (10)$$

possible combinations if the number of O atoms is  $n$ . If we compare two ethers in the pure form, one containing  $x$  O atoms per molecule and the other containing  $n$  O atoms per molecule, then the former ether contains approximately  $n/x$  times more molecules per unit volume than the latter. The efficiency of the latter ether relative to the former with respect to the solvation of  $K^+$  should therefore be multiplied with a factor  $x/n$ . In the latter case (eqn. (10)) we get:

$$(n-x+1)\frac{x}{n} = x - \frac{x^2-x}{n} \quad (11)$$



Eqn. (11) indicates that when  $n$  increases the efficiency for  $K^+$  solvation approaches an upper value which equals  $x$  times the efficiency of the ether with  $x$  oxygen atoms ( $x$  is the coordination number).

It should be noted that the above consideration of a combination of possibilities may also be applied if more than one molecule takes part in the primary solvation of one  $K^+$  ion. The only restriction is that the number of glycol ether molecules taking part in the solvation of the  $K^+$  ion is constant (independent of the chain length).

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