THE DECOMPOSITION OF TRIETHYL SULPHONIUM BROMIDE IN MIXED SOLVENTS.

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The kinetics of the decomposition of triethyl sulphonium bromide in a number of single solvents have been investigated very thoroughly by von Halban.¹ Subsequent work by Taylor and Lewis² has shown that there is satisfactory agreement between the infra-red absorption bands, observed spectroscopically, and those calculated from the critical increments derived from von Halban's data. All the available evidence goes to show that the decomposition of triethyl sulphonium bromide follows a simple unimolecular equation. It is therefore a convenient reaction to employ in connection with the influence of environment upon the rate of chemical change.

An account is here given of the results obtained with certain mixed solvents which serve at the same time to bring out a point of some importance in connection with the relation which exists between reaction rate and critical increment of activation.

Experimental.

Two series of experiments have been carried out. In the one, the solvent was benzyl alcohol plus glycerol, in the other, benzyl alcohol plus toluene. Glycerol and toluene were used because of their widely different physical properties (*e.g.*, viscosity and dielectric constant) and also because both liquids are miscible in all proportions with benzyl alcohol.

The triethyl sulphonium bromide was prepared at the outset by the method of Taylor and Lewis,² but this mode of preparation proved to be long and tedious. The salt was therefore prepared by maintaining a mixture of ethyl sulphide and ethyl bromide at a temperature of 38.4° C. (this temperature being slightly below the boiling-point of ethyl bromide) for seven days. The crystals of triethyl sulphonium bromide, which had formed, were then purified from ethyl bromide and ethyl sulphide by precipitating the salt from alcoholic solution by means of ether. The crystals were kept in a vacuum desiccator pending use.

The method used in following the reaction was similar to that of von Halban, *i.e.*, by introducing a definite volume of the salt in the solvent under investigation into a number of test-tubes, the latter being then sealed off. The amounts of solution used varied from 2 c.c. for the more concentrated solutions, to 5 c.c. for the less concentrated solutions. It is interesting to note that, whereas the addition of glycerol increased the

¹Z. physikal. Chem., 67, 129, 1909.

² Trans. Chem. Soc., **121**, 665, 1922. 41

solubility of the sulphonium bromide, the addition of toluene decreased the solubility of the salt. All the test-tubes were then immersed in a thermostat at the most suitable temperature (previously determined), in this case 80° C. and 90° C. respectively and, at the beginning of the reaction and subsequently at regular intervals during the course of the reaction, a test tube was withdrawn, cooled in ice and the unchanged triethyl sulphonium bromide estimated by shaking the contents with a mixture of ether and water in a separating funnel. The aqueous layer, containing the unchanged triethyl sulphonium bromide, was then separated and the ethereal layer washed twice with water to ensure complete extraction of the sulphonium bromide. The latter was finally estimated by addition of excess standard silver nitrate and back-titration of the latter with standard ammonium thiocyanate.

The benzyl alcohol used was first dried over anhydrous sodium sulphate and redistilled, the portion used distilling at 206° C. The glycerol was distilled at 15 mm. pressure at 190° C., the glycerol distilling thus without any decomposition. Toluene was dried over sodium wire for twentyfour hours and redistilled, the portion used distilling at 110° C. at 760 mm. The solutions under investigation, containing high concentrations of glycerol, were measured out by weight instead of by volume.

The composition of the benzyl alcohol + glycerol mixtures used in the first series of experiments is given in Table I. The benzyl alcohol-toluene mixtures used in the second series are given in Table IV.

In general, the reaction in organic solvents reaches an end point which corresponds with the complete decomposition of the salt. With pure glycerol as solvent, however, no sensible decomposition can be observed.

It was found that the addition of glycerol to benzyl alcohol caused a displacement of the point of equilibrium between reactant (triethyl salt) and resultants indicated by the equation :---

$$(C_2H_5)_3SBr \rightleftharpoons (C_2H_5)_2S + C_2H_5Br$$

towards the side of the reactant, *i.e.*, in the direction characteristic of the equilibrium in pure glycerol solution itself. Consequently it was found necessary to determine equilibrium constants for the reaction in the different benzyl alcohol + glycerol mixtures at both temperatures. These were found by maintaining a known volume of the solution of triethyl sulphonium bromide in the given solvent at the temperature required until equilibrium was attained. The time of immersion was in all cases ten times the period of half decomposition of the sulphonium bromide. The initial and equilibrium concentrations of the sulphonium bromide were determined in the manner previously outlined, the values of the equilibrium constants being given by the expression :—

$$\mathbf{K} = \frac{(\mathbf{C}_2\mathbf{H}_5)_3\mathbf{SBr}}{(\mathbf{C}_2\mathbf{H}_5)_2\mathbf{S} \times \mathbf{C}_2\mathbf{H}_5\mathbf{Br}}$$

The concentrations are expressed in moles per litre in every case. Table I. gives the values of K for each solvent at the two temperatures.

The expression for the unimolecular velocity constant was then corrected for a bimolecular reverse reaction as follows. If we denote the initial concentration of triethyl sulphonium bromide by a mols. per litre and the amount decomposed after a time t by x, we obtain :

$$-\frac{dx}{dt} = k_1(a - x) - k_2 x^2$$

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	Composition	n of Solvent.					
Mass Per Cent.		Molar Per Cent.		К ₈₀ °.	K ₉₀ °.	Q (Heat Absorbed in Dissociation	
Benzyl Alcohol.	Glycerol.	Benzyl Alcohol.	Glycerol.	-		of the Salt.)	
100'00 90'23 80'39 69'39	0.00 9.77 19.61 30.61	100°00 88°74 77°74 65°46	0.00 11.20 22.20 34.24	1•64 4·91 14·32 42·49	1.22 3.70 11.10 34.01	7,500 7,200 6,500 5,700	

TABLE I.

where k_1 and k_2 are the rates of the forward and reverse reactions respectively. Since $K = k_2/k_1$, we obtain :

$$k_1 = \frac{1}{tC} \log \frac{(1 - C)(2Kx + 1 + C)}{(1 + C)(2Kx + 1 - C)} \text{ where } C = \sqrt{1 + 4aK}.$$

As an instance of the applicability of this equation, the uncorrected and corrected velocity constants at 90° C. using benzyl alcohol containing 34.54 molar per cent. glycerol are given in Table II.

t (Mins.).	$\begin{array}{c} (a - x) \\ \text{C.c. NH}_4 \text{CNS.} \end{array}$	(a - x) Mols./Litre.	$k_{\rm obs} imes$ 10 ⁵ .	<i>k</i> _{corr} × 10 ⁵ .
0	18.61	0.08496	0.844	
230	16.56	0.07560	0.875	
408	15.02	0.06857	0.828	
572	14.02	0.06400	0.766	
702	13.48	0.06155	0.756	
819	12.83	0.05857	0.644	
1112	12.11	0.05530	Iean 0.785	

TABLE II.

The final values of the corrected velocity constants in benzyl alcohol + glycerol mixtures are given in Table III., time being expressed in seconds and logarithms to the base e. In the case of benzyl alcohol + toluene mixtures, Table IV., no correction is necessary as the reaction goes to completion.

TABLE III.

Solvent. Molar Per Cent.		$k_{30}^{\circ} \times 10^{5}$.	$k_{90}^{\circ} \times 10^{5}$.	E in Cals. Per Mole.	
Benzyl Alcohol.	Glycerol.				
100°00 88'74 77'74 65'46	0.00 11.26 22.26 34.54	1'480 0'720 0'444 0'233	6°075 2°83 1°695 0°882	35,900 34,800 34,100 33,900	

The reaction velocities were determined in duplicate in every case, but only the mean values are quoted.

Discussion of Results.—Considering the effects of glycerol and toluene respectively on the velocity of decomposition, it will be observed that, whereas the addition of glycerol causes a progressive lowering of the velocity constant, the addition of toluene causes a progressive increase.

Solver Molar Per	ıt. Cent.	$k_{80}^{\circ} \times 10^5$.	$k_{90} \times 10^{5}$.	E in Cals. Per Mole
Benzyl Alcohol.	Toluene.			
100'00	0.00	1.480	6.075	35,900
75 25 50'34 25'26	49.66 74.74	7.796 24.45	28·59 88·32	33,100 32,700

INDED IV.	TA	BLE	IV.
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From the observed velocity constants, the critical increments for the decomposition in the various solvents can be calculated by means of the equation,

$$\frac{d \log k}{dt} = \frac{\mathrm{E}}{\mathrm{RT}^2}.$$

Values of E thus calculated have been included in Tables III and IV.

Assuming that a unimolecular reaction consists of the spontaneous decomposition of the activated reactant, the general expression for the unimolecular velocity constant takes the form $k = Se^{-E/RT}$. If S is independent or approximately independent of the physical properties of the mixed solvents, we would expect that an increase in the velocity constant would be accompanied by a decrease in the critical increment. This is so in the case of benzyl alcohol + toluene mixtures, the addition of toluene causing an increase in k and a diminution in E. In the case of benzyl alcohol + glycerol mixtures, on the other hand, as the velocity constant falls, the calculated critical increment also falls. The addition of glycerol to the solvent would appear therefore to introduce an "anomaly" in either the observed velocity constants or the apparent critical increments. The fact that in both series of solvents an appreciable variation in the apparent critical increments is observed would suggest that the stability of the triethyl sulphonium bromide molecule is altered by the addition of toluene and glycerol respectively. Such a variation in stability should manifest itself in the infra-red absorption bands of the sulphonium bromide in the solvents employed. This conclusion does not imply that the chemical change is due to absorption of radiation. The measurement of the infra-red absorption bands and the treatment of the "anomaly" from the point of view of infra-red absorption spectra is taken up in the next section.

The Infra-Red Absorption Spectra of Triethyl Sulphonium Bromide in the Different Solvent Mixtures.

From the magnitude of the observed critical increments, it was expected that a characteristic absorption band would lie in the very short wave-length region of the infra-red, a region in which it is difficult to measure absorption bands with accuracy.

The method and precautions employed in the determination of the absorption bands were those of Taylor and Lewis² with the modification that the radiomicrometer was replaced by a thermopile and Moll Galvano-

The latter instrument meter. proved to be very efficient although it was extremely susceptible to atmospheric conditions. The greatest difficulty experienced in the present work was that the intensity of light of wave-lengths between 0.7μ and 1.00μ was small, and consequently a high degree of accuracy was necessary in the readings of the deflexions of the galvanometer. The absolute magnitude of the deflection was of the order 3 to 7 cms. and the change therein for 0.2μ change in wave-



cent. benzyl alcohol.

length corresponded with 0.3 - 0.5 cm. approximately.



FIG. 2.—Composition of solvent, 88.74 per cent. benzyl alcohol + 11.26 per cent. glycerol.



FIG. 3.—Composition of solvent, 77.74 per cent. benzyl alcohol + 22.26 per cent. glycerol.



FIG. 4.—Composition of solvent, 65'46 per cent. benzyl alcohol + 34'54 per cent. glycerol.



FIG. 5—Composition of solvent, 75°25 per cent, benzyl alcohol + 24°75 per cent. toluene.



FIG. 6.—Composition of solvent, 50'34 per cent. benzyl alcohol + 49'66 per cent. toluene.



FIG. 7.—Composition of solvent, 25.26 per cent. benzyl alcohol + 74.74 per cent. toluene.

The solubility of the triethyl sulphonium bromide in the solvents is of the order of tenth normal with respect to the solute and consequently the variations in the percentage transmission at the head of the band, and away from the band, are not great. They are, however, sufficiently distinct to identify without doubt the position of the band. The accompanying curves, Figs. 1-7, give the absorption bands for the different solvents (full lines) and solutions (broken lines) over the range $0.70\mu - 1.20\mu$.

Tables V. and VI. give the values of the observed wave-lengths of the band head and also the wave-lengths calculated from the equation $E = Nh\nu$. where E is the observed critical increment obtained from the temperature coefficient of the reaction velocity constants, and in the last column the critical increment regarded as the true increment calculated from the actual position of the band head.

Solvent. Molar Per Cent.		Ecalcd.	Wave-Length (Calcd.)	Wave-Length	F	
Benzyl Alcohol.	Glycerol.	Coeff.	(from Previous Column).	(Obs.).	L'true.	
100°00 88°74 77°74 65°46	0°00 11°26 22°26 34°54	35,900 34,800 34,100 33,900	0°79µ 0°81µ 0°83µ 0°84µ	0°78µ 0°76µ 0°74µ 0°72µ	36,300 37,100 38,200 39,500	

TABLE V.

TABLE VI.

Solvent. Molar Per Cent.		Ecaled.	Wave-Length (Calcd.)	Wave-Length	F.	
Benzyl Alcohol.	Toluene.	Coeff.	(from Previous Column).	(Obs.).	~uue.	
100°00 75°25 50°34 25°26	0°00 24'75 49'66 74'74	35,900 34,800 33,100 32,700	0.79µ 0.81µ 0.85µ 0.87µ	0°78µ 0°80µ 0°82µ 0°84µ	36,300 35,400 34,600 33,700	

Considering first the results for the benzyl alcohol + toluene mixtures, it will be seen that the agreement between the observed wave-length and that calculated from the critical increment as given by the temperature coefficient is fairly good, bearing in mind the experimental difficulties, and we may therefore conclude that in benzyl alcohol + toluene mixtures, the stability of the triethyl sulphonium bromide molecule is equally well expressed by the absorption band and by the critical increment of decomposition, as obtained from the temperature coefficient.

For the case of the benzyl alcohol + toluene mixtures it is of interest to calculate the value of S which occurs in the general type equation $k = \text{Se}^{-E/\text{RT}}$, the values of E being those given in the final column of Table VI. and k the observed velocity constant at 80° C. (Table IV.), to see whether S alters appreciably or not. In the case of a unimolecular process S has the dimension of time⁻¹. The following results are obtained.

Molar	per cent.	of to	oluene	:	0.0	24.75	49.66	74.74
S × 1	o - 17	•	•	•	4.57	2.77	2.12	1.81

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It will be observed that S remains of the same order of magnitude throughout. Whether the fall in the values is significant or not it is difficult to say, for the total change in S lies within the experimental error of the values ascribed to E_{true} . (Thus in order to alter S from 1.81×10^{17} to 4.57×10^{17} it is only necessary to assume that E = 34,300 calories in place of the value actually employed, *viz.* 33,700, or otherwise expressed, the position of the band head required is 0.83μ instead of the observed value 0.84μ .)

The first inference to be drawn from the approximate constancy of the S values is that volume concentration terms of the triethyl salt (which have been employed in the determination of the k values) are legitimate quantities to use, or in other words that the activity values in this case—if activity be involved—may be replaced by such terms. (Incidentally activity values based on solubility would have led to values of k which would in turn have required greater variation in S.)

The second inference to be drawn is that the magnitude of S, of the order 10^{17} , is so very great that it cannot be attributed to any frequency term characteristic of any type of motion within the molecule which would be likely to be involved in chemical change in the ordinary sense. It follows therefore that S is not a single term but rather the product of two or more. Incidentally this value of S is many times greater than that found for the unimolecular decomposition of nitrogen pentoxide in certain organic solvents, namely of the order 10^{14} , which is likewise characteristic of unimolecular reaction in the gaseous state.

In the benzyl alcohol + glycerol mixtures, it will be seen that the addition of glycerol causes a progressive shift in the infra-red absorption band towards shorter wave-lengths. Moreover as the glycerol concentration increases, the divergence between the observed and the calculated infra-red wave-lengths (obtained from the temperature coefficient of the reaction velocity) becomes more pronounced. The absorption spectra indicate that the effect of glycerol differs from that of toluene in that it renders the molecule of the triethyl salt more stable, whereas the addition of toluene renders it less stable. The relative positions of the band head taken as a measure of stability would lead us to expect that in the case of the benzyl alcohol + glycerol mixtures the velocity of decomposition of the triethyl salt should decrease with increase in glycerol content, a conclusion in agreement with experiment. In this case, therefore, the anomaly between critical increment and velocity constant reduces to a failure of the observed velocity constants to give a true value for the critical increment.

The writer has not succeeded in obtaining a satisfactory explanation of the effect referred to. A number of possibilities have been considered, for example the introduction of a viscosity term (which necessitated the determination of the viscosities of the various mixtures at the reaction temperatures), the introduction of considerations based on dielectric constant (since it is reasonable to believe that the relative amounts of the polar (ionisable) and non-polar form of the triethyl salt would depend upon the dielectric capacity and it is the non-polar form which alone decomposes into alkyl halide and sulphide) and the possible formation of glycerol-triethyl None of these possibilities, however, in so far as the salt complexes. writer has been able to deal with them, seem capable of altering the relative positions (with increasing glycerol content) of the velocity constant curves at two different temperatures in the direction required to account for and eliminate the anomaly, namely the conversion of the slight convergence actually exhibited by the curves into a small divergence such as is required by the general downward trend of the velocity constant curve

(at a given temperature) as well as by the observed positions of the band head in the various solvent mixtures.

The only fact which seems to bear even indirectly upon the difference in behaviour of glycerol and toluene respectively in relation to triethyl sulphonium bromide is that the addition of glycerol (to benzyl alcohol) increases the solubility of the salt whilst the addition of toluene decreases the solubility.

Leaving aside the problem of attempting to account for the anomaly referred to, it appears reasonable to conclude that the positions of the band heads in the short infra-red region afford in the present case the most reliable values for the true critical increments. These values calculated from the band heads are recorded in the final columns of Tables V. and VI.

The calculation of the S term in the case of benzyl alcohol + glycerol mixtures shows that this term increases fairly rapidly with increase in glycerol content. Thus in the absence of glycerol $S = 4.57 \times 10^{17}$ whilst with 34.54 molar per*cent. $S = 6.88 \times 10^{18}$. This variation is real in that it lies outside the experimental error involved in the band head measure-(Thus in order to convert the latter value of S into the ment of E_{true}. former, it would be necessary to take E = 37,600 calories ($\lambda = 0.755\mu$) instead of E = 39,500 (λ = 0.72 μ observed.)

The Effect of the Removal of Dust on the Velocity of Decomposition of Triethyl Sulphonium Bromide in Propyl Alcohol.

In a recent paper, F. O. Rice³ has shown that, in a number of reactions, studied by him, dust particles ordinarily present in all solutions exert a marked catalytic activity. For example the decomposition of hydrogen peroxide in aqueous solution and the oxidation of sodium sulphite are almost completely suspended when special care is taken to remove the dust from the solution.

In view of this it was considered of interest to determine the rate of decomposition of triethyl sulphonium bromide in a suitable organic solvent, namely propyl alcohol, both solvent and solution being freed as far as possible from dust and the reaction carried out in an atmosphere of dust free air.

Experimental.

Dust Free Solvent.-The dust free solvent was prepared by the distillation method of Martin⁴ which has been employed by Rice and found to be satisfactory. The distillation and rinsing process was repeated, on the average, nine times, in order to ensure that the liquid finally in the bulb was dust free. The amount of dust was observed qualitatively by concentrating an intense beam of light from an arc lamp on the vessel and Examination of the solution after each disobserving the Tyndall effect. tillation showed that the amount of dust decreased until, after about nine distillations, the liquid was entirely dust free, as far as the method of observation could ascertain.

Dust Free Air .- The method of preparation of 'dust free' air was essentially that of Dewar,⁵ and was based on the fact that when a current of air is passed through a vessel containing cotton wool previously saturated with glycerol, the latter removes dust from the air.

 ³ J. Amer. Chem, Soc., 48, 2099, 1926.
⁴ J. physical Chem., 24, 478, 1920.
⁵ Proc. Roy. Inst., 22, 179, 1918.

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A current of air was passed through three towers, the first containing a mixture of lime and anhydrous sodium carbonate, the second containing soda lime and the third closely packed cotton wool, previously thoroughly saturated with glycerol. The first tower removed water vapour, the second carbon dioxide and the third dust from the air passing through them. Examination by the Tyndall cone method, of the air itself and of a purified solvent through which the air was drawn showed that this method was satisfactory since no evidence of dust was found in the air treated in the above manner.

Dust Free Solutions .- In the first place it was necessary to have the solid solute freed from dust. This was done by suspending the solute in dry ether in a vessel which was eventually joined to the principal apparatus and passing a current of dry, dust free air through the mixture. The agitation caused by the passage of the gas removed the dust from the solute and this was carried away in the ether vapour with the current This procedure was repeated four times and the resulting solid of air. sulphonium bromide taken as 'dust free'. The solid salt was shaken into the reaction vessel, the operation being carried out in an atmosphere of dust The resulting solution was shown to be 'dust free' by the Tyndall free air. cone test. The reaction vessel was fitted with a tap, through which portions of the liquid could be extracted for analysis at intervals during the run. Lubricating grease could not be used, the tap being surrounded by a vessel of mercury. Whilst still connected to the supply of dust free air, the whole apparatus was immersed in a thermostat at the temperature of investigation, in this case 80° C., and the reaction followed in the manner previously described. The solution was extracted via the tap and the volume of solution was replaced by a quantity of dust free air, so that no dust was introduced into the reaction vessel during the various readings. The results below give the velocity constants using solutions largely freed from dust and also using solutions of triethyl sulphonium bromide in propyl alcohol from which no attempt was made to remove dust.

Solvent.			Expt. No.	k ₈₀ ° × 10 ⁵ .
Propyl alcohol containing dust """"""""""""""""""""""""""""""""""""	• • •	• • •	I II III IV V	2·748 2·756 2·739 2·743 2·750

TABLE VII.

The values recorded in the above table are the same, within the limits of experimental error. This case is therefore apparently analogous to the 'unimolecular' gaseous reaction examined by Rice and shown to be independent of the presence of dust. Whether this feature is general or not is unknown. It may be pointed out that the results of the dust removal experiments afford no clue to the anomaly dealt with earlier in this paper.

Summary.

r. The unimolecular velocity constants of the decomposition of triethyl sulphonium bromide into diethyl sulphide and ethyl bromide have been determined at 80° C. and 90° C. in mixed solvents containing benzyl alcohol + toluene and benzyl alcohol + glycerol respectively. The presence

of glycerol causes the reaction to reach an equilibrium point. The corresponding equilibrium constants at 80° C. and 90° C. have been determined and with their aid a corrected velocity constant of decomposition obtained. It is found that whilst the toluene increases the rate of decomposition the glycerol decreases it.

2. From the temperature coefficients of the reaction it is found that the (apparent) critical increments of activation fall in value as the content of either toluene or glycerol in the benzyl alcohol is increased. The direction of change in the case of benzyl alcohol + toluene mixtures is therefore that which would be anticipated on theoretical grounds in view of the observed change in the velocity constant with solvent composition. On the other hand the behaviour in benzyl alcohol + glycerol mixtures is anomalous.

3. With the object of throwing some light on the anomaly the absorption spectra exhibited by the triethyl salt in the short infra-red region in the various solvent mixtures have been determined by means of a Hilger infra-red spectrometer, Moll galvanometer and thermopile. It is found that the position of the head of the band varies with the composition of the In the case of benzyl alcohol + toluene mixtures the shift in the solvent. position of the band head is in satisfactory agreement with the alteration in the observed critical increment. In the case of benzyl alcohol + glycerol mixtures the head of the band shifts towards the shorter wave-length whilst the change calculated from the critical increment is in the opposite The direction of shift of the band is that which would be direction. expected from the effect of glycerol upon the velocity constant (at a given temperature). It is concluded therefore that the band head gives the true critical increment.

4. The decomposition of triethyl sulphonium bromide in propyl alcohol has been investigated under conditions which permit of the extensive removal of the dust ordinarily present in all solutions. It is shown that no effect is produced upon the velocity of decomposition, the behaviour in this case being analogous to that found by F. O. Rice for the (unimolecular) decomposition of gaseous nitrogen pentoxide.

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