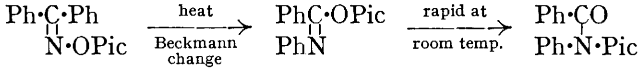
337. *Studies of the Beckmann Change. Part II. The Kinetics of the Spontaneous Rearrangement and Solvent Effects.*

By Arthur W. Chapman.

In Part I (J., 1933, 806) it was shown that the picryl and related ethers of ketoximes undergo a spontaneous Beckmann rearrangement when heated alone or in suitable solvents, *e.g.*,



$$\text{(I.)}\ \begin{matrix}\text{Ph·C·Ph}\\ \| \\ \text{N·OPic}\end{matrix} \xrightarrow[\text{Beckmann change}]{\text{heat}} \begin{matrix}\text{PhC·OPic}\\ \| \\ \text{PhN}\end{matrix} \xrightarrow[\text{room temp.}]{\text{rapid at}} \begin{matrix}\text{Ph·CO}\\ | \\ \text{Ph·N·Pic}\end{matrix}\ \text{(II.)}$$

and that the transformation, which follows a unimolecular course, is complete and without measurable by-products. The change does not require an external catalyst except in so far as the solvent might be regarded as such, nor does it depend on the action of light, and reasons were adduced for regarding the rearrangement as an intramolecular exchange of positions by the picryloxy and the hydrocarbon radical.

The velocity of transformation is, however, greatly affected by the solvent, and before a systematic study of substituted oxime ethers was begun, a further investigation of the kinetics of the change seemed desirable. This has now been carried out with benzophenone oxime picryl ether (I) as the substance undergoing rearrangement.

The results described in Part I showed that, under otherwise similar conditions, the velocity of the change increases in the same order as the dielectric constant of the solvent; *i.e.*, that the transformation is facilitated by an environment of polar molecules. Measurements in any one solvent were, however, made at one concentration only, and, as both the oxime ether and its change product contain strongly polar groups, it seemed likely that the rate of change would also be affected by the concentration of the solution, especially in non-polar solvents.

A series of velocity measurements has therefore been carried out on solutions of the oxime ether in carbon tetrachloride. The results are given in Table I. [Concentrations (*c*) are in g.-mol. per l. of solution at the particular temperature employed, times in secs. ; Napierian logarithms.] The highest concentrations approach the saturation point at room temperature.

TABLE I.

Temp.		Concentration and velocity.				$k_0 \times 10^5$.	$x \times 10^5$.
70·5°	c		0·0228				
	$k \times 10^5$		1·84			(1·17)	—
80·5°	c	0·0112	0·0223	0·0286	0·0303		
	$k \times 10^5$	5·14	5·87	6·37	6·41	4·40	67
81·0°	c	0·0118	0·0225		0·0348		
	$k \times 10^5$	5·53	6·30		6·76	4·73	67
85·9°	c	0·0112			0·0333		
	$k \times 10^5$	9·55			12·74	7·9	—
91·2°	c	0·0112			0·0326		
	$k \times 10^5$	16·4			21·6	13·7	—
92·8°	c	0·0110	0·0222		0·0334		
	$k \times 10^5$	18·9	21·0		23·1	16·8	190
100·0°	c	0·0109	0·0223		0·0328		
	$k \times 10^5$	38·4	43·0		46·8	34·1	392

From these results it is clear that the concentration of the solution exerts an important influence on the rate of rearrangement. Since the unimolecular velocity constant remained steady throughout the whole course of the transformation, the catalytic activities of the oxime ether and of its change product must be nearly identical. The velocity constants at any one temperature fall upon a straight line when plotted against the concentration of the solution, and the relationship between these values can thus be expressed by the equation $k = k_0 + xc$, where k_0 is the coefficient at infinite dilution, and x the increase of velocity for a concentration of 1 g.-mol./l. The values of k_0 at all temperatures studied, and for x at all temperatures at which three or more determinations were made, are given in Table I.

The rate of change of the oxime ether in carbon tetrachloride is therefore composed of two factors : the velocity at which the change would occur at infinite dilution (k_0), and an additional velocity, proportional to the concentration of the solution, arising from the catalytic effect of the oxime ether and its product on the rearrangement.

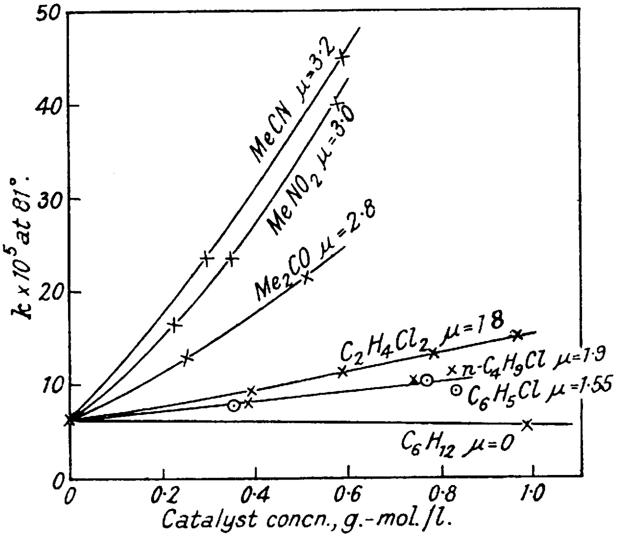
At infinite dilution the oxime ether molecules can only be activated by collision with solvent molecules. The values of log (k_0/η) when plotted against $1/T$ fell upon a straight line corresponding with a value of 30,250 cals. per g.-mol. for the critical increment of the rearrangement (k_0/η was used instead of k_0 since the frequency of solvent–solute collisions in any one solvent is proportional to the viscosity of the solvent). The rates of change actually observed were about 20 times as great as those calculated from this value of the critical increment and the frequencies of collision between carbon tetrachloride and oxime ether molecules derived from the accepted formulæ (Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, p. 28).

The values of log x plotted against $1/T$ also fell on a straight line, corresponding in this case with a value for E of 22,620 cals. per g.-mol. If it be assumed that the catalysed change is brought about by collisions between molecules of the ether with other molecules of the ether or with those of the change product, then on the accepted assumptions as to collision frequency (Moelwyn-Hughes, *op. cit.*, p. 16), the observed values of x lie between 0·4 and 0·5 of those demanded by the theory.

The difference between the critical increments of the catalysed and the uncatalysed rearrangement is considerable, and it must be concluded that, whilst collision of an oxime ether molecule with one of carbon tetrachloride will cause rearrangement if it involves more than a certain amount of energy, a definitely smaller energy increment will suffice to bring about the transformation when the oxime ether molecule is activated by or in the neighbourhood of another molecule of the same sort or of its change product.

This conclusion can be simply explained in terms of the following hypothesis regarding the mechanism of the catalysis. The migration of the picryloxy and the hydrocarbon group between the nitrogen and carbon atoms of the oxime picryl ether must involve some degree of dissociation of their original linkages, and the amount of energy necessary to bring this dissociation about will largely determine the ease with which migration takes place. Since the dissociation involves the development of electrical charges at the ends of the bonds concerned, it will require less energy when the process can take place within a suitably oriented field provided by another molecule than when it occurs in a non-polar environment. Whilst, therefore, the oxime ether molecules rearrange with difficulty when surrounded solely by non-polar molecules of carbon tetrachloride,* the change will take place with increasing ease as the meeting of two strongly polar solute molecules becomes more and more frequent with rising concentration of the solution.

According to this hypothesis, polar compounds of any kind should catalyse the change in the order of the strength of the dipoles in their molecules. A further study of the effects of different solvents on the rate of rearrangement has therefore been undertaken. The experimental method employed was to measure the rate of change in a standard solution of the oxime picryl ether in carbon tetrachloride containing a known quantity of the second solvent. This procedure permitted observations to be made at different concentrations of the catalytic solvent and also the use of a much wider range of catalysts than would have been possible had the oxime ether been dissolved in each of the different pure solvents in turn. The main features of the results are shown in the fig., which illustrates measurements made at 81°, including a series on ethylene dichloride, which contains two principal dipoles in the molecule. It will be seen that the catalytic activities of the different substances are in the same order as their dipole moments, rising very rapidly at the higher values of the dipole moment. The catalytic effect of *cyclo*hexane is zero within the limits of experimental error.



At the relatively high concentrations employed, the effects of the more powerful catalysts increased with rising concentration more rapidly than would be required by a linear relationship, but, within the limits of these experiments, the connexion between the velocity of the change and the concentration of the catalyst could be expressed by an equation of the form $k = k_{\text{un.}} + xC + yC^2$, where $k_{\text{un.}}$ is the velocity in the absence of a catalyst, C the catalyst concentration, and x and y are constants for the catalyst employed. The values of x represent the catalytic activities at high dilutions and furnish a basis for numerical comparisons at different temperatures and between different catalysts. These values are given in Table II.

The critical increments (obtained in each case from the values of x at three temperatures) of the catalysed rearrangement brought about by nitromethane and ethylene dichloride were 23,800 and 24,400 cals. per g.-mol. respectively. These again are definitely lower than the

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* Whether carbon tetrachloride itself exerts any catalytic influence on the change in the sense of this hypothesis cannot be determined exactly. The effect in any case, however, must be small, and the behaviour of the oxime ether in carbon tetrachloride has therefore been taken as the standard for comparison of solvent effects.

value for the uncatalysed transformation, but somewhat higher than that for catalysis by the oxime ether itself. When combined with the estimated collision frequencies, they lead to values of x, for nitromethane approximately twice, and for ethylene dichloride four times, as great as those actually observed.

TABLE II.

Catalyst.	MeCN.	$MeNO_2$.	Me_2CO.	n-C_4H_9Cl.	$C_2H_4Cl_2$.	C_6H_5Cl.	C_6H_{12}.	Oxime ether on itself.
$\mu \times 10^{18}$.........	3·2	3·0	2·8	1·9	1·8	1·55	0·0	—
$x \times 10^5$ at 81·0°	52	36·5	25	5·3	6·8	5·4	−0·8	67
70·5	—	13·3	—	—	—	—	—	—
91·0	—	—	—	—	17·8	—	—	—
92·8	—	118	—	—	—	—	—	190
100·0	—	—	—	—	40·5	—	—	392

So far, therefore, the results obtained agreed with the view put forward to explain the existence of the catalysis. A further test of this view, however, seemed possible. If the catalytic effect of the solvent upon the rearrangement of the oxime ether is essentially due to the action of the field of the catalyst molecule on the ether, then certain substances which have no molecular dipole moment should be capable of accelerating the transformation. Compounds in which a zero dipole moment is due to the presence of two or more equal and opposite dipoles in the molecule should act as catalysts provided that the two dipoles be far enough apart. Two such dipoles occurring close together may be expected to neutralise one another so far as any external field of the molecule is concerned. On the other hand, when sufficiently separated, the two fields should function more or less independently, and the compound containing them should thus be able to act as a catalyst although causing little or no change in the dielectric constant of the medium in which the rearrangement takes place.

To test this deduction, three compounds of zero dipole moment were employed, each containing two separate carbon–halogen dipoles. Their catalytic activities were measured at 81° and compared with those of ethylene dichloride and of a polar isomeride of each substance. The results are summarised in Table III.

TABLE III.

Substance.	$x \times 10^5$ at 81°.	$\mu \times 10^{18}$.	Substance.	$x \times 10^5$ at 81°.	$\mu \times 10^{18}$.
trans-Dichloroethylene	1·1	0·0	*cis*-Dichloroethylene	5·9	1·8
p-Dichlorobenzene	2·9	0·0	*m*-Dichlorobenzene	4·7	1·5
trans-1 : 4-Dibromo*cyclo*hexane	5·5	0·0 *	*cis*-1 : 4-Dibromo*cyclo*hexane	10·5	—
Ethylene dichloride	6·8	1·8			

* μ shown to be zero by Halmöy and Hassel (*Z. physikal. Chem.*, 1932, **15**, *B*, 472).

In *trans*-dichloroethylene the two dipoles are relatively close together and the catalytic effect of this substance is very small, whilst the *cis*-compound behaves like ethylene dichloride. The catalytic activity of *p*-dichlorobenzene is somewhat less than, but of the same order as, that of its *m*-isomeride, and *trans*-1 : 4-dibromo*cyclo*hexane is almost as efficient a catalyst as ethylene dichloride. The prediction as to the behaviour of these compounds is therefore completely fulfilled. The high catalytic activity of *cis*-1 : 4-dibromo*cyclo*hexane may perhaps be due to the strong field which this compound will have in certain configurations of its flexible molecule.

The results of the present study may therefore be summarised as follows :

1. The Beckmann rearrangement of an oxime picryl ether dissolved in a non-polar solvent such as carbon tetrachloride proceeds, under suitable conditions of temperature, at a measurable rate even at very low concentration.

2. The velocity of change is affected markedly by the presence in the solution of any of a wide variety of materials which resemble one another only in containing polar groups within their molecules, and include the oxime ether itself and its change product.

3. The catalytic activities of compounds which contain one principal dipole fall in the same order as the dipole moments of the substances.

4. Compounds that contain equal and opposite dipoles in each molecule and are there-

fore non-polar still exhibit catalytic activity when the dipoles are sufficiently separated. When the opposing dipoles are close together catalytic activity is inappreciable.

5. The critical increment of the catalysed change depends on the catalyst and is definitely lower than that of the rearrangement in pure carbon tetrachloride at infinite dilution.

6. These concentration and solvent effects can all be explained in terms of the suggested catalytic mechanism.

EXPERIMENTAL.

Benzophenone oxime picryl ether was prepared and purified as described in Part I.

Solvents and Catalysts.—Commercially pure carbon tetrachloride was redistilled, with rejection of the first and last sixths; it then boiled over a range of not more than 0·2°. Acetonitrile and ethylene dichloride were purified as described in Part I. The sample of acetone used had been digested with sodium hydroxide and potassium permanganate and redistilled. Nitromethane, *n*-butyl chloride, chlorobenzene, and *cyclo*hexane were purified by repeated distillation of commercial specimens. *p*-Dichlorobenzene was purified by recrystallisation; m. p. 52—54°. *m*-Dichlorobenzene was obtained from 2 : 4-dichloroaniline and repeatedly redistilled under reduced pressure.

cis- and *trans*-1 : 4-Dibromo*cyclo*hexanes were obtained by heating *cyclo*hexane-1 : 4-diol with 8 times its weight of fuming hydrobromic acid (*d* 1·7) under reflux on the steam-bath until no more oil was deposited from the liquid (cf. Baeyer, *Annalen*, 1894, **278**, 94). The *trans*-compound was separated from the oily mixture by freezing out, and was twice recrystallised from alcohol (m.p. 112—114°). The *cis*-compound was washed with dilute alkali, dried, and repeatedly fractionated under reduced pressure; b. p. 119—121°/18 mm.

cis- and *trans*-Dichloroethylenes were obtained by fractional distillation of the commercial mixture. The final products had b. p.'s respectively 58—60° and 48—49·5°, and dielectric constants (kindly determined by Mr. D. P. Earp) 8·814 and 3·286 at 20°; comparison of these values with those given for the pure substances (*cis*-, 9·22; *trans*-, 2·25 at 20°; " International Critical Tables," **6**, 84) indicated that the specimen of *cis*-compound contained 5·5% of *trans*-isomeride, and the *trans*- 14·5% of *cis*-.

Catalysts with one principal dipole, at 81°.

Catalyst.		Concentration and velocity.					$x \times 10^5$.	$y \times 10^5$.
MeCN	C	0·00	0·292	0·588				
	$k \times 10^5$	6·30	23·4	45·0			52	24
$MeNO_2$	C		0·221	0·343	0·574			
	$k \times 10^5$		16·25	23·5	40·0		36·5	39
Me_2CO	C		0·250	0·507				
	$k \times 10^5$		13·2	21·6			25	9·5
C_4H_9Cl	C		0·384	0·735				
	$k \times 10^5$		8·18	10·17			5·3	—
C_6H_5Cl	C	0·00	0·353	0·764				
	$k \times 10^5$	6·03	7·68	10·29			5·4	—
C_6H_{12}	C	0·00	0·985					
	$k \times 10^5$	6·30	5·53				−0·8	—

Catalytic activity of nitromethane at different temperatures.

Temp.		Concentration and velocity.				$x \times 10^5$.	$y \times 10^5$.
70·5°	C	0·00	0·354	0·694	1·04		
	$k \times 10^5$	1·84	8·0	17·3	29·1	13·3	13
81·0	C	0·00	0·221	0·343	0·574		
	$k \times 10^5$	6·30	16·25	23·5	40·0	36·5	39
92·8	C	0·00	0·089	0·175			
	$k \times 10^5$	21·0	32·2	44·1		118	80

Catalytic activity of ethylene dichloride at different temperatures.

81·0	C	0·00	0·389	0·584	0·778	0·964		
	$k \times 10^5$	6·30	9·22	11·1	13·0	14·9	6·8	2·4
91·0	C	0·00	0·304	0·575	0·792			
	$k \times 10^5$	17·9	23·8	29·5	36·1		17·8	6·1
100·1	C	0·00	0·148	0·267	0·376			
	$k \times 10^5$	44·3	50·5	55·8	60·8		40·5	9·3

Catalysts with two principal dipoles per molecule at 81°.

Catalyst.		Concentration and velocity.					$x \times 10^5$.	$y \times 10^5$.
$C_2H_2Cl_2$	C	0·00	0·396	0·793				
$\epsilon^{20°} = 3{\cdot}286$	$k \times 10^5$	6·30	7·1	7·6			1·8	—
		Corrected value for pure *trans*-compound $\epsilon^{20°} = 2{\cdot}25$.					1·1	—
p-$C_6H_4Cl_2$	C	0·00	0·463	0·628				
	$k \times 10^5$	6·03	7·22	7·87			2·9	—
$C_6H_{10}Br_2$	C	0·00	0·316	0·582				
trans	$k \times 10^5$	6·03	8·06	9·25			5·5	—
$C_2H_4Cl_2$	C	0·00	0·389	0·584	0·778	0·964		
	$k \times 10^5$	6·30	9·2	11·1	13·0	14·9	6·8	2·4
$C_2H_2Cl_2$	C	0·00	0·407	0·813				
$\epsilon^{20°} = 8{\cdot}814$	$k \times 10^5$	6·30	9·4	13·5			5·6	3·0
		Corrected value for pure *cis*-compound $\epsilon^{20°} = 9{\cdot}22$.					5·9	—
m-$C_6H_4Cl_2$	C	0·00	0·308	0·538	0·672			
	$k \times 10^5$	6·03	7·1	9·2	9·2		4·7	—
$C_6H_{10}Br_2$	C	0·00		0·185	0·265	0·382		
cis	$k \times 10^5$	6·03		8·49	9·88	13·1	10·5	15

Velocity Determinations.—For solutions in carbon tetrachloride alone or containing catalysts of b. p. up to 100°, the method for carbon tetrachloride solutions described in Part I was used.

For the analysis of solutions containing chlorobenzenes or dibromo*cyclo*hexanes, the following technique was employed. Exactly 25 c.c. of solution were introduced into each reaction tube and sealed up. After heating, the tube was opened, and the contents transferred to a small beaker containing as seed a weighed amount (0·2—0·4 g.) of powdered benz-*N*-picrylanilide (II), and the tube was washed out into the beaker with 25 c.c. of a saturated solution of benz-*N*-picrylanilide in carbon tetrachloride. The beaker was then kept in a desiccator over the same solution for not less than 2 hours to allow the mixture to come to equilibrium. The contents were stirred at intervals, and the desiccator was nearly immersed in running water to keep the temperature steady. When equilibrium had been attained, the contents of the beaker were filtered through a fritted-glass filter crucible, and the solid residue washed with a saturated solution of benz-*N*-picrylanilide (100 c.c.), dried at 100—120°, and weighed. The residue on the filter consisted of the original seed together with all the benz-*N*-picrylanilide formed from the oxime ether in excess of the small amount required to saturate the original oxime ether solution. The method was tested on a solution in pure carbon tetrachloride and gave a value for k 4—5% lower than that obtained by the ordinary technique. This was adopted as the zero value for experiments carried out in this way.

Determinations of the catalytic activities of all solvents were carried out on solutions containing 1 g. of oxime ether per 100 c.c. of solution at room temperature ($0{\cdot}0225M$ at 81°).

Results of Velocity Determinations.—These are recorded in the table above. t is given in secs., and C in g.-mol. per l. at the temperature of the experiment.

Calculated Values for Collision Frequencies at 81°.

σ, oxime ether $= 9{\cdot}18 \times 10^{-8}$ cm.; σ, $CCl_4 = 6{\cdot}12 \times 10^{-8}$ cm; σ, $MeNO_2 = 5{\cdot}0 \times 10^{-8}$ cm.; σ, $C_2H_4Cl_2 = 5{\cdot}72 \times 10^{-8}$ cm. Collisions per second between one molecule of oxime ether and solvent molecules, calculated from the formula $Z = 3\pi\eta\sigma(M_1 + M_s)/2mM_s$: $Z = 1{\cdot}10 \times 10^{13}$; $Ze^{-30,250/RT} = 2{\cdot}24 \times 10^{-6}$; k_0, obs. $= 4{\cdot}73 \times 10^{-5}$.

Collisions per second between one molecule of the oxime ether and other molecules of the same in a solution containing 1 g.-mol. per l., calculated from the formula $Z = \sigma^2 n\sqrt{4\pi RT/M}$: $Z = 1{\cdot}54 \times 10^{11}$; $Ze^{-22,620/RT} = 156 \times 10^{-5}$; x, obs. $= 67 \times 10^{-5}$.

Collisions per second between one molecule of oxime ether and catalyst molecules in solutions containing 1 g.-mol. of catalyst per l., calculated from the formula $Z = \sigma_{1,2}^2 n_2\sqrt{8\pi RT(1/M_1 + 1/M_2)}$:

(*a*) for $MeNO_2$: $Z = 3{\cdot}61 \times 10^{11}$; $Ze^{-23,800/RT} = 69 \times 10^{-5}$; x, obs. $= 36{\cdot}5 \times 10^{-5}$.

(*b*) for $C_2H_4Cl_2$: $Z = 3{\cdot}28 \times 10^{11}$; $Ze^{-24,400/RT} = 26 \times 10^{-5}$; x, obs. $= 6{\cdot}8 \times 10^{-5}$.

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