Anal. Calcd. for $C_{14}H_{14}O_7$: C, 57.14; H, 4.80. Found: C, 57.30; H, 5.07. Mol. wt. calcd.: 294. Found (cryoscopic in benzene): 307.

Approximately the same ratio of dimer to monomer was obtained when the hydrolytic rearrangement was carried out under nitrogen or carbon dioxide in 0.1N hydrochloric acid which had boiled to expel dissolved air.

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Beckmann Rearrangement. III. Rearrangement of Oxime *p*-Toluenesulfonates in Chloroform, Acetic Acid, and Methanol

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The ΔE_a and $\Delta S^{\ddagger}$ in the rearrangement of several oxime p-toluenesulfonates in chloroform, acetic acid, and methanol were determined. The rearrangement is fastest in methanol > acetic acid ≫ chloroform. The rate constant of the reaction in acetic acid decreases in the following sequence: cyclohexanone > benzophenone ≅ cycloheptanone ≅ cyclooctanone > cyclopentanone ≅ acetophenone > acetone. The rearrangement is believed to proceed with the formation of an azacyclopropene ring system in the transition state. Acid catalysis increases the rate of rearrangement in chloroform but decreases the rate in acetic acid.

Much work has been done on the mechanism of the Beckmann rearrangement and several reviews[1] summarize the published literature on the reaction.

Essentially, the rearrangement proceeds by intramolecular migration of the group "anti" to the departing $OR^{\ominus}$ group. Furthermore, Chapman[2] found that the rate of rearrangement increases with an increasing dielectric constant of the solvent. A study of the salt effects and the acetolysis of cyclopenta- and cyclohexanone oxime p-toluenesulfonates described in the previous paper[3] suggested a stable transitory ion pair which apparently contains an azacyclopropene ring system.

This paper describes the influence of solvent, structure, and acid catalysis upon the Beckmann rearrangement of oxime p-toluenesulfonates.

EXPERIMENTAL

Acetolysis of cycloalkanone oxime p-toluenesulfonates was measured as described previously[3] by titration of the p-toluenesulfonic acid formed. Acetic acid solutions were prepared by dissolving 1 g. of water weighed to ±1 mg. in 10 g. of 100% acetic acid, weighed to ±10 mg. and diluting this solution to the concentration indicated in Table I by means of a calibrated buret. The standard sodium acetate solution was prepared in the same solvent as that prepared for the reaction medium of each run. If the water concentration in acetic acid exceeded 0.35M, the 0.1% Bromphenol Blue solution could not be used as an indicator because of the sluggish color change. A solution of perchloric acid in 100% acetic acid was prepared according to the method of Kolthoff.[4] To a known amount of dry silver perchlorate in 100% acetic acid was added standard hydrochloric acid solution, prepared by bubbling dry hydrogen chloride into 100% acetic acid. The silver chloride was filtered off, and the resulting perchloric acid solution was standardized against sodium acetate. Each run was measured by titrating eight to ten fresh batches of the tosylate at increasing time intervals with standard sodium acetate. The rates were evaluated from the first order rate equation to about 80% reaction.

TABLE I

EFFECT OF (A) WATER AND (B) PERCHLORIC ACID ON THE RATE CONSTANT OF ACETOLYSIS OF CYCLOPENTANONE OXIME p-TOLUENESULFONATE

(Temp. = 35.55 ± 0.05°)

Oxime Tosylate mequiv.	Added	Mg.	Mequiv.	$k \times 10^{+4}$ sec.$^{-1}$
0.79	—	—	—	6.06
0.79	H_2O	20.4	1.11	5.80
0.79	"	40.0	2.22	5.89
0.79	"	80.4	4.44	6.29
0.79	"	160.0	8.88	6.06
0.79	"	400.0	22.22	6.13
0.79	$HClO_4$	8.5	0.085	4.49
0.79	"	42.4	0.424	4.03
0.79	"	84.4	0.847	3.64
0.79	"	169.4	1.694	3.74
0.79	"	248.1	2.481	2.69

Rate of solvolysis of oxime p-toluenesulfonates in methanol, ethanol, and alcohol-water mixtures were followed by titration of the p-toluenesulfonic acid formed with standard sodium methoxide or sodium ethoxide to $pH = 8.0$, using a pH-meter and a Bartlett-Swain titration cell equipped with a calomel- and a glass-electrode.[5] The standard solution consisted of the same solvent mixture as a solution in the titration cell. The rates followed the first order equation up to about 80% of complete reaction. The results are summarized in Tables II and III.

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[1] (a) A. H. Blatt, *Chem. Rev.*, **12**, 215 (1933); (b) B. Jones, *Chem. Rev.*, **35**, 335 (1944); (c) I. L. Knunyants and B. P. Fabrichnyi, *Usepckhi Khimi*, **18**, 633 (1949); (d) L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, XI, 1 (1960).

[2] D. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936).

[3] W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5972 (1958).

[4] I. M. Kolthoff and W. William, *J. Am. Chem. Soc.*, **56**, 1007 (1934).

[5] P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

TABLE II

INFLUENCE OF ETHANOL-WATER MIXTURES UPON THE RATE OF SOLVOLYSIS OF CYCLOHEXANONE OXIME p-TOLUENESULFONATE

Solvent	Temp., ±0.05°	Rate Constant, sec.$^{-1}$	ΔE_a kcal.	$\Delta S^{\#}$, e.u.
100% C_2H_5OH	0.45	2.65×10^{-5}	22.6	(+)1.2
	15.8	2.40×10^{-4}	±1.2	(±)2.5
	29.15	1.37×10^{-3}		
90% C_2H_5OH-10% H_2O (By weight)	0.55	1.68×10^{-4}	19.5	(−)6.4
	13.3	8.3×10^{-4}		
80% C_2H_5OH-20% H_2O (By weight)	0.75	7.35×10^{-4}	18.2	(−)8.2
	13.60	3.3×10^{-3}		

TABLE III

DETERMINATION OF THERMODYNAMIC QUANTITIES IN THE METHANOLYSIS OF OXIME p-TOLUENESULFONATES

Oxime p-Toluenesulfonates	Temp., ±0.05°	$k \times 10^{+4}$ sec.$^{-1}$	Est'd. Mean Deviation	ΔE_a, kcal.	$\Delta S^{\#}$, e.u.	$\Delta F^{\#}$, kcal., at 25°
Benzophenone	19.65	6.70	0.45	20.9	(−)3.6	21.4
	24.05	11.17		(±)1.6	(±)2.6	
	28.08	19.81	1.33			
Cyclopentanone	35.05	3.99	0.17	24.4	(+)3.2	22.8
	39.80	8.22		(±)1.1	(±)2.5	
	49.80	24.6	1.7			
Cyclohexanone	0.50	1.74	0.12	17.9	(−)12.0	20.5
	5.00	2.94		(±)1.1	(±) 3.4	
	13.35	7.57	0.50			
Cycloheptanone	13.35	1.78	0.12	20.1	(−)7.4	21.7
	17.65	2.88		(±)1.5	(±)2.9	
	24.10	6.38	0.43			
Cyclooctanone	13.35	2.03	0.13	17.4	(−)16.6	21.7
	17.70	3.22		(±)1.5	(±) 3.0	
	24.30	6.24	0.42			

TABLE IV

REFERENCE SPECTRA OF CYCLOALKANONE OXIME p-TOLUENESULFONATES IN CHLOROFORM

Run No.	1	2	3	4	5	6
A. Cyclopentanone oxime p-toluenesulfonate						
Tosylate, mg.	93	56	45	41	23	19
$CHCl_3$, g.	2.297	2.027	1.906	2.526	2.610	2.729
Molality of tosylate	0.16	0.109	0.093	0.060	0.035	0.027
Absorbance at 867 cm.$^{-1}$	0.63	0.445	0.395	0.260	0.155	0.112
B. Cyclohexanone oxime p-toluenesulfonate						
Tosylate, mg.	79	70	60	41	31	21
$CHCl_3$, g.	2.025	2.047	2.027	2.000	2.013	2.108
Molality of tosylate	0.148	0.131	0.112	0.077	0.058	0.039
Absorbance at 857 cm.$^{-1}$	0.545	0.475	0.435	0.295	0.223	0.140
C. Cycloheptanone oxime p-toluenesulfonate						
Tosylate, mg.	95	66	45	35	25	15
$CHCl_3$, g.	2.006	2.004	2.004	2.047	2.036	2.011
Molality of tosylate	0.169	0.117	0.080	0.062	0.042	0.026
Absorbance at 837 cm.$^{-1}$	0.730	0.535	0.355	0.272	0.195	0.148

Rate determination. The kinetics of the rearrangement of oxime p-toluenesulfonates in chloroform were determined spectrophotometrically with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer. Sodium chloride cells were used in all analytical determinations. The cells were standardized according to the Fringe Method.[6] The instrument settings during each run were: Resolution = 9.6; Response = 1.0; Gain = 6.0; Speed = 4.0; Suppression = 0; and Scale = 1/1. Reference samples of each oxime p-toluenesulfonate in chloroform were prepared and the concentration determined by the Base-Line method.[7] The following bands of oxime p-toluenesulfonates obeyed Beer's Law and were used in the determination of the concentrations of sulfonate esters: 867 cm.$^{-1}$, cyclopentanone; 857 cm.$^{-1}$, cyclohexanone; 837 cm.$^{-1}$, cycloheptanone and cyclooctanone. Reference plots for these compounds are given in Table IV. The calibration curves in chloroform could also be used for calculating concentrations in trichloroethane and tetrachloroethane. The disappearance of the bands at 867 cm.$^{-1}$, 857 cm.$^{-1}$, and 837 cm.$^{-1}$ followed the first order rate equation. The rates were calculated from the usual first order equation[8]:

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad (1)$$

where k = rate constant, t = time, a = oxime derivative present at zero time, and x = rearranged material present.

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(6) D. C. Smith and E. C. Miller, *J. Opt. Soc. Am.*, **34**, 130 (1944).

(7) J. J. Heigel, M. F. Bell, and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

The following is a typical run: 770 mg. of cyclohexanone oxime p-toluenesulfonate was dissolved in 20 g. of freshly purified chloroform.[9] Twenty-five tubes were filled with an equal amount of the solution and were sealed. The usual sealed tube technique was then carried out. A detailed example is summarized in Table V.

TABLE V

DETERMINATION OF THE RATE CONSTANT OF REARRANGEMENT OF CYCLOHEXANONE OXIME p-TOLUENESULFONATE IN CHLOROFORM

Samples, 770 mg. (2.08 mmoles), of tosylate in 20 g. of chloroform were sealed in separate tubes. Bath temperature was 49.9 ± 1.0°. Tubes were chilled in Dry Ice after withdrawal from constant temperature bath.

Time, sec.	% Reaction	Absorbance	Log $\frac{a}{a-x}$	$k \times 10^{+4}$ sec.$^{-1}$
0	0	0.43	—	3.66
300	11	0.385	0.04766	2.72
600	15	0.365	0.07115	2.94
900	23	0.33	0.11494	3.30
1200	33	0.29	0.17114	2.74
1500	37	0.27	0.20222	2.92
1800	41	0.255	0.22943	3.29
2100	50	0.215	0.30103	3.29
2400	55	0.195	0.34341	3.32
2700	59	0.175	0.39041	3.41
3000	64	0.155	0.44311	3.39
3300	67	0.14	0.48728	3.32
3600	70	0.13	0.51957	3.48
3900	74	0.11	0.59207	3.45
4200	77	0.10	0.63347	3.59
4500	80	0.085	0.70406	3.87
4800	84	0.07	0.78838	3.68
				Avg. 3.34 ± 0.20

The reaction was first order up to about 80% completion. The average mean deviation in the specific example cited was ±0.20 or ±6%, which was about typical for all determinations. Energies of activation, ΔE_a, were determined from the Arrhenius equation and $\Delta S^{\#}$, were calculated from the absolute rate theory.[8]

$$\log k = \log A - \frac{\Delta E_a}{2.303RT} \tag{2}$$

and

$$\log k = \frac{KT}{h} - \frac{\Delta E_a}{2.303RT} + \frac{\Delta S^{\#}}{2.303R} \tag{3}$$

where k = rate constant at temperature T; A = Arrhenius frequency factor; E_a = energy of activation; R = gas constant; T = absolute temperature; K = Boltzmann's constant; and h = Planck's constant.

Although the reproducibility of the analytical method after some practice had a relative error of about ±2%, the rate data are believed to have a relative error of about ±4%, mainly due to the reading of the indicator. The deviations in ΔE_a, and $\Delta S^{\#}$ resulting from a ±6% relative error were calculated from the Taft[10] equations:

$$\Delta E_a = \frac{RT_1T_2}{T_2 - T_1} \ln\left(\frac{k_2}{k_1}\right) \pm \frac{RT_1T_2}{T_2 - T_1}\left[\left(\frac{r_2}{k_2}\right)^2 + \left(\frac{r_1}{k_1}\right)^2\right]^{1/2} \tag{4}$$

and

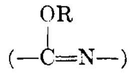
$$\Delta S^{\#} = \frac{RT_2 \ln k_2 - RT_1 \ln k_1}{T_2 - T_1} - R \ln\left(\frac{KT}{h}\right) - R \pm \frac{R}{T_2 - T_1}\left[\left(T_2\frac{r_2}{k_2}\right)^2 + \left(T_1\frac{r_1}{k_1}\right)^2\right]^{1/2} \tag{5}$$

where R = gas constant; K = Boltzmann's constant; h = Planck's constant; T_2, T_1 = the maximum and minimum temperatures, respectively, in °K.; k_2, k_1 = rate constants at T_2 and T_1, respectively; r_2, r_1 = mean deviations in k_2, k_1. The ΔE_a and $\Delta S^{\#}$ calculated in this manner are summarized in Tables III, VI, and VII.

RESULTS AND DISCUSSION

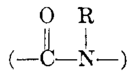
Rearrangement in chloroform. The rates of the Beckmann rearrangement of cyclopentanone (I), cyclohexanone (II), cycloheptanone (III), and cyclooctanone (IV) oxime p-toluenesulfonates in chloroform were measured. The rate of rearrangement of I was measured by disappearance of the band at 867 cm.$^{-1}$ Although the absorbance of several bands (1602 cm.$^{-1}$; 1455 cm.$^{-1}$; 1369 cm.$^{-1}$; 1180 cm.$^{-1}$; 1167 cm.$^{-1}$; and 848 cm.$^{-1}$) of I decreased with the progress of rearrangement, none of these bands obeyed Beer's Law as well as the band at 867 cm.$^{-1}$ Apparently, intermediates formed in the reaction contribute in some degree to the bands in question. The disappearance of the band at 867 cm.$^{-1}$ for I followed the first order equation quite well up to about 80% reaction. The average mean deviation of the rate constant was in most cases ±6%, but in some cases ±10%.

Kuhara[11] found that the Beckmann rearrangement proceeds through an imine intermediate,



$(-\overset{\overset{\displaystyle OR}{|}}{C}=N-)$

which rearranges to the N-substituted amide.



$(-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R}{|}}{N}-)$

Unfortunately, attempts to prepare O-(p-toluenesulfonyl)caprolactim (II$_b$) and a sample or pure N-(p-toluenesulfonyl)caprolactam (II$_c$) failed and the kinetics of the individual steps (II → II$_b$ → II$_c$) could not be evaluated quantitatively.[12] As the rearrangement progressed, several bands gradually appeared in the infrared spectrum of II, which could belong to II$_b$ since their intensity decreased with the progress of the reaction (1660 cm.$^{-1}$, 1250 cm.$^{-1}$, 1120 cm.$^{-1}$, 1032 cm.$^{-1}$, 1102 cm.$^{-1}$). In addition, a very sharp band appeared

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[8] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, New York (1953).

[9] J. W. Williams and F. Daniels, *J. Am. Chem. Soc.*, **46**, 903 (1924).

[10] E. L. Purlee, R. W. Taft, and C. A. Defazio, *J. Am. Chem. Soc.*, **77**, 837 (1955).

[11] M. Kuhara, K. Matsuimya, and N. Matsunami, *Mem. Coll. Sci., Kyoto Imp. Univ.* **1**, 105 (1914); *Chem. Abstr.*, **9**, 1613 (1915).

[12] W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880 (1958).

TABLE VI

Determination of Thermodynamic Quantities in the Acetolysis of Oxime *p*-Toluenesulfonates

Oxime *p*-Toluene-sulfonate	Temp., ±0.05°	$k \times 10^{+4}$ sec.$^{-1}$	Est'd. Mean Deviation	ΔE_a, kcal.	$\Delta S^{\ddagger}$, e.u.	$\Delta F^{\ddagger}$, kcal., at 25°
Acetone	37.60	0.0844	0.0015	23.4	(−)8.0	25.2
	51.70	0.503		(±)0.6	(±)2.3	
	60.80	1.16				
	70.50	3.19	0.06			
syn-Methylacetophenone	18.85	0.904	0.02			22.5
	28.00	3.45		22.8	(−)1.0	
	38.45	15.6		(±)0.6	(±)2.3	
	51.60	62.6	1.30			
Benzophenone	21.50	5.87	0.31	21.9	(−)1.2	21.7
	35.90	31.6		(±)0.6	(±)1.9	
	39.85	48.82	2.01			
Cyclopentanone	24.50	1.39	0.057	23.4	(+)0.4	22.7
	30.70	2.83		(±)0.6	(±)2.3	
	35.82	6.56				
	40.00	10.46	0.43			
Cyclohexanone	18.35	14.5	0.63	19.1	(−)8.0	20.9
	21.00	18.4		(±)0.7	(±)2.3	
	26.90	36.8				
	35.75	91.2	5.0			
Cycloheptanone	24.50	7.12	0.29	20.6	(−)5.5	21.6
	30.80	13.52		(±)0.9	(±)2.3	
	35.90	29.25				
	39.75	38.12	1.60			
Cyclooctanone	24.80	7.46	0.31	19.1	(−)10.7	21.7
	30.80	15.80		(±)1.0	(±)2.2	
	35.90	23.49				
	39.70	45.60	1.88			

TABLE VII

Determination of Thermodynamic Quantities in the Rearrangement of Oxime *p*-Toluenesulfonates in Chloroform

Oxime *p*-Toluene-sulfonate	Temp., ±0.10°	$k \times 10^{+4}$ sec.$^{-1}$	Est'd. Mean Deviation	ΔE_a, kcal.	$\Delta S^{\ddagger}$, e.u.	$\Delta F^{\ddagger}$, kcal., at 25°
Cyclopentanone	79.8	1.05	0.06	27.0	(−)1.5	27.0
	89.5	2.92		(±)1.3	(±)3.4	
	96.5	6.01	0.34			
Cyclohexanone	39.9	0.78	0.042	23.4	(−)4.7	24.2
	49.9	2.90		(±)1.1	(±)2.7	
	60.0	7.78				
	70.1	21.90	1.04			
Cycloheptanone	59.0	0.838	0.049	24.4	(−)6.1	25.6
	69.1	2.27		(±)1.1	(±)2.6	
	79.7	7.21	0.409			
Cyclooctanone	63.2	1.70	0.096	21.8	(−)13.0	25.6
	69.1	2.92		(±)1.2	(±)3.4	
	79.1	7.74	0.44			

at 2330 cm.$^{-1}$ The band at 2330 cm.$^{-1}$ apparently belonged to a side product which formed from II in an unexplained manner. The formation of the side product was apparently accelerated by impurities on the walls of the tubes. (When the glass tubes were boiled in cleaning solution for a long time prior to use, this band did not appear.) Final product of the rearrangement, believed to be II$_c$, had a characteristic band at 1710 cm.$^{-1}$ Qualitatively, the half-life of I → I$_b$ was in the same order of magnitude as that of I$_b$ → I$_c$ as estimated qualitatively from a combination of infrared spectra and acetolysis of partially rearranged reaction mixtures.[3,13] As the ring size of the parent oxime was increased from I to IV, the half-life of the intermediate lactim decreased as compared to the half-life of the starting material. When IV was rearranged in chloroform, the carbonyl band of the substituted lactam at 1725 cm.$^{-1}$ appeared immediately as IV began to rearrange, and the lactim intermediate had apparently only transitory existence. The infrared spectra of three reaction mixtures of II at different time intervals are represented in Fig. 1.

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(13) It appears that the sequential steps in the rearrangement could be studied by a combination of spectrophotometric and titrametric methods.

TABLE VIII

INFLUENCE OF SOLVENT ON THE RATE CONSTANTS OF REARRANGEMENT OF OXIME *p*-TOLUENESULFONATES (Temp. = 25°)

Oxime *p*-Toluenesulfonate	Solvent	k	k_{AcOH}/k_{CHCl_3}	k_{CH_3OH}/k_{AcOH}	m
Cyclopentanone	Chloroform	7.55×10^{-8}	1907	0.8	—
	Acetic acid	1.44×10^{-4}			
	Methanol	1.09×10^{-4}			
Cyclohexanone	Chloroform	1.08×10^{-5}	276	1.0	0.58
	Acetic acid	2.99×10^{-3}			
	Methanol	3.02×10^{-3}			
	Ethanol	8.26×10^{-4}			
	90% Ethanol-10% water[a]	3.15×10^{-3}			
	80% Ethanol-20% water[a]	1.23×10^{-2}			
Cycloheptanone	Chloroform	1.01×10^{-6}	656	1.1	—
	Acetic acid	6.63×10^{-4}			
	Methanol	7.46×10^{-4}			
Cyclooctanone	Chloroform	2.53×10^{-6}	303	0.9	—
	Acetic acid	7.67×10^{-4}			
	Methanol	6.95×10^{-4}			
Benzophenone	Acetic acid	8.62×10^{-4}	—	1.5	
	Methanol	1.31×10^{-3}			

[a] Mixtures are by weight.

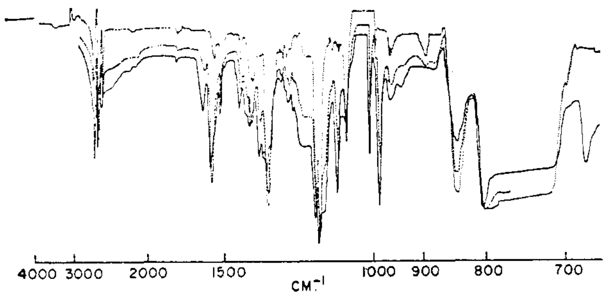

Fig. 1. Rearrangement of cyclohexanone oxime *p*-toluenesulfonate in chloroform at 49.9 ± 0.05°. ······ 0 min.; ------ 60 min.; ——— 100 min.

Solvent effects. The rate constant of solvolysis of an oxime *p*-toluenesulfonate in a solvent is a function of the ionizing power, Y, of the solvent and its nucleophilic power, N.[14–16] Thus, the rate constant of solvolysis may be expressed as[14b]:

$$d \log k = \left(\frac{\partial \log k}{\partial N}\right)_Y dN + \left(\frac{\partial \log k}{\partial Y}\right)_N dY \quad (6)$$

In solvents of comparable nucleophilicity such as alcohol-water mixtures, $dN \cong 0$ and the Grunwald-Winstein free energy relationship is obtained.[14a,16] Where k = rate constant of solvolysis

$$\log (k/k_0) = \mathrm{m}Y = -\frac{1}{2.303RT}\left(\frac{\partial \Delta F^{\ddagger}}{\partial Y}\right) Y \quad (7)$$

of *tert*-butyl chloride in a solvent, k_0 = rate constant of *tert*-butyl chloride in a standard solvent, Y = ionizing power of the solvent, and m = constant characteristic of *tert*-butyl chloride. The structural constant "m" may also be expressed as the variation of $\Delta F^{\ddagger}$ due to ionizing power of the solvent. $\Delta F^{\ddagger}$ includes terms which relate to the solvation of RX in the ground state, transition state and due to solvent-solvent interactions.[16] In Beckmann rearrangements, the reaction medium is frequently diethyl ether or chloroform.[1d] Therefore, it should be useful to employ a measure of ionizing power which extends into these solvents. Kosower's "Z" values[17] may be used in this connection.[18] Table VIII summarizes the influence of several solvents on the rate of rearrangement of oxime *p*-toluenesulfonates at 25°. In alcohol-water mixtures where $dN \cong 0$, a structural constant m = 0.58 is obtained, when the rate of alcoholysis of II is plotted versus Y. The relative high "m" indicates a small but definite contribution of

$$\left(\frac{\partial \log k}{\partial N}\right)_Y$$

to the rate of solvolysis of II in alcohol and aqueous alcohol.[19]

In Fig. 2, the rate constants for the rearrangement of II *vs.* Kosower's "Z" values are plotted. A reasonable linear correlation is obtained which indicates that the rate of solvolyses of II in acetic acid is considerably faster than the Grunwald-Winstein-Kosower relationship would predict. In Column 5, Table VIII is summarized the ratio

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[14] (a) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 846 (1945); (b) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

[15] S. Winstein, A. H. Fainberg, and E. Grunwald. *J. Am. Chem. Soc.*, **79**, 4146 (1957).

[16] S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

[17] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

[18] S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

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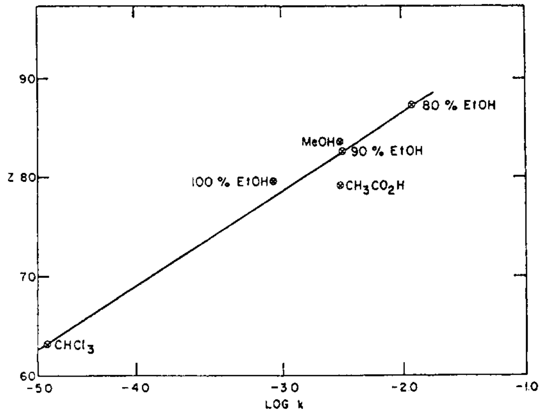

* "Z" value for CHCl$_3$ refers to CHCl$_3$ containing 0.13M. EtOH

Fig. 2. Linear relationship of Kosower's "Z" values with the log k of cyclohexanone oxime p-toluenesulfonate in various solvents

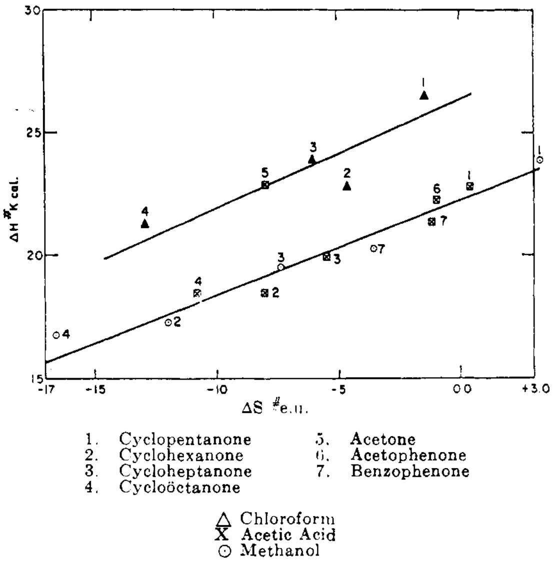

Fig. 3. Isokinetic temperatures of oxime p-toluenesulfonates in chloroform, acetic acid, and methanol

k_{CH_3OH}/k_{AcOH} which is approximately one for all oxime p-toluenesulfonates investigated, although the solvolytic and presumably nucleophilic power of methanol is greater than that of acetic acid. The rate of acetolysis appears to be enhanced by specific acetic acid interactions with the ground and/or transition state. The rate constant in acetic acid could be increased either by the addition of a proton to the oxygen of the oxime (see below) or by specific interactions between the leaving p-toluenesulfonate ion and the acetic acid solvent. If rate enhancement was solely due to the former case no large differences in primary salt effects could be expected among the oxime p-toluenesulfonates such as have been observed previously.[3] Apparently, the rate enhancement of oxime p-toluenesulfonates in acetolyses is mainly due to a solvent interaction with the leaving p-toluenesulfonate ion. A similar large positive deviation from the rate predicted by the Grunwald-Winstein correlation was observed by Swain in the acetolyses of triphenylmethyl fluoride which may be ascribed to interaction between the leaving fluoride ion and acetic acid.[19a,b] An extensive discussion on the electrophilic assistance to ionization by hydrogen bonding is given by Winstein.[19]

In Table VIII, Column 4, are given $k_{AcOH}/k_{CHCl_3} = Z_{(AcOH\ =\ 79.2)}/Z_{(CHCl_3\ =\ 63.2)}$ as a rough measure of the solvent ionizing power in acetic acid as compared to chloroform. The k_{AcOH}/k_{CHCl_3} ratio is larger for I and III than for II and IV. This appears to mean that, especially for I but also for III, the higher rate constant in acetic acid is due to a greater dissociation of the N—O bond in the transition state (or transitory complex). In II and IV, the driving force for the rearrangement appears to be due to two factors: a lesser degree of dissociation of the N—O bond of the oxime, and a greater degree of the neighboring group (N.G.) participation of the migrating methylene group. This viewpoint is augmented by the small acceleration of the rate of acetolysis of I by the "normal salt" effect as compared to the large acceleration of the rate of acetolysis of II by the same effect.[3] In the case of I, lack of acceleration indicates a relatively dissociated transition state (or transitory intermediate) in pure acetic acid, and in the case of II, a lesser dissociated transition state (or transitory intermediate).

An examination of the thermodynamic quantities in Tables III, VI, and VII is very revealing. $\Delta F^{\neq}$ varies relatively little from compound to compound in a given solvent. On the other hand, ΔE_a and $\Delta S^{\neq}$ vary far beyond the experimental errors inherent in the data. Furthermore, a plot (Fig. 3) of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ yields a linear correlation characteristic of each solvent.[16,20,21] The poorest correlation is found when oxime p-toluenesulfonates are rearranged in chloroform. The only compound which does not appear to fit its isokinetic temperature is the acetolysis of acetone oxime p-toluenesulfonate (V). The slope of the plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$, Leffler defined as the "isokinetic temperature."[20] The isokinetic temperature for chloroform is 402°K. and for acetic acid and methanol is 404°K. or well above the average experimental temperature. This linear isokinetic relationship probably indicates grossly similar mechanisms or transition states in each of the solvents investigated.[20] The nearly parallel displacement of the kinetic temperatures from chloroform to acetic acid and methanol by about 3.5–4.0 kcal. is probably due to specific solvent influences on the ground and transition states of the oxime p-toluenesulfonates

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(20) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

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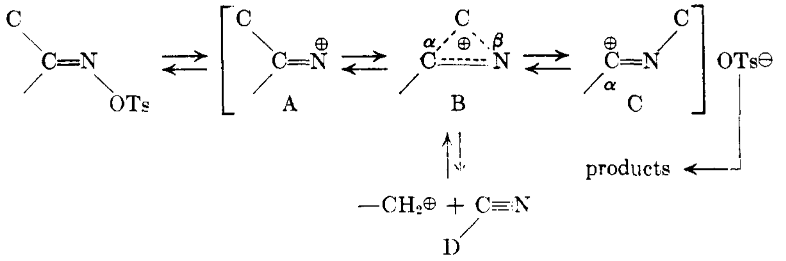
inherent in the heat of solvation of the ground and transition states. It is of interest to note that no displacement of the isokinetic temperatures is observed when acetic acid is replaced by methanol; the only effect of methanol is a linear displacement $\Delta H^{\neq}$ toward lower $\Delta H^{\neq}$ and of $\Delta S^{\neq}$ toward lower $\Delta S^{\neq}$. The only exception observed is I, where the reverse is true.

Structural effects. The rate constant of the acetolysis of oxime *p*-toluenesulfonates decreases in the following sequence (see Table VIII, Column 2): cyclohexanone > benzophenone ≅ cycloheptanone ≅ cyclooctanone > acetophenone > acetone. If the assumption of a basically similar reaction mechanism may be made (see above), it may be useful to inquire into the reasons for such a sequence.

The rate constant, and therefore, $\Delta F^{\neq}$, will be determined by the difference between the ground and transition states for each oxime. The transition state for the Beckmann rearrangement may be discussed as a function of structure[22]:



(8)

and as a function of the degree of ionization and dissociation[23]:

$$\underset{1}{\mathrm{RX}} \rightleftharpoons \underset{\substack{\text{Intimate}\\ \text{ion pair}\\ 2}}{\mathrm{R}^{\oplus}\mathrm{X}^{\ominus}} \rightleftharpoons \underset{\substack{\text{Solvent separated}\\ \text{ion pair}\\ 3}}{\mathrm{R}^{\oplus}\,\|\,\mathrm{X}^{\ominus}} \rightleftharpoons \underset{\substack{\text{Dissociated}\\ \text{ions}\\ 4}}{\mathrm{R}^{\oplus} + \mathrm{X}^{\ominus}} \tag{9}$$

The rate constant (at 25°) of acetolysis for a sequence of oxime *p*-toluenesulfonates increases in the following fashion: acetone (1) < acetophenone (160) < benzophenone (670). The increase of the rate constants is in the correct direction of migratory aptitude of phenyl as compared to methyl group in the Wagner-Meerwein rearrangement.[24] Unfortunately, there appears to be no study reported in which rate of ionization of the N—O bond of an oxime ester was studied in a system which excludes N.G. participation, *i.e.*, rearrangement such as antiindanone oxime[25] or fluorenone oxime *p*-toluenesulfonate,[1d] and, therefore, a direct comparison with the migratory aptitudes of Wagner-Meerwein rearrangement with the Beckman rearrangement cannot be made. Nevertheless, data obtained by other workers[25] indicate that the difference between the migratory aptitude of phenyl and methyl should be much greater than actually observed. The phenyl group in benzophenone will stabilize the charge at C_α in the transition state[2] and will thusly increase the rate of rearrangement.[26] On the other hand, the ground state in benzophenone will be stabilized by resonance interaction of the C=N bond with the aromatic ring system which in turn will increase the energy necessary for favorable perpendicular rearrangement of the aromatic ring in relation to the double bond or the azacyclopropene ring system in the transition state, thusly cause a large decrease in the rate constant.[25,27] The ratio of rate constants in acetolysis of benzophenone as compared to acetophenone (provided that both have the same transition states in acetolysis) may serve as an approximate measure of the resonance stabilization of the ground state attributed to the phenyl and methyl groups: $k_{\text{benzophenone}}/k_{\text{acetophenone}} \cong 4$ at 25°.

The large deviation of V from the isokinetic temperature of acetolysis (Fig. 3) may indicate that its acetolysis proceeds with a different mechanism or (more probably) by a different transition state from the others. Since the methyl group is a rather poor N.G. participant, the transition state may be represented probably by structures similar to A (Equation 8).

The sequence in the rate constants for cyclopentanone < cyclohexanone > cycloheptanone ≦ cyclooctanone was explained by Brown[28] and Pearson[29] in terms of I-strain theory. This theory

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(22) R. Huisgen, J. Witte, and W. Jira, *Ber.*, **90**, 1850 (1957).

(23) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chemistry and Industry*, 664 (1954).

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(26) D. J. Cram in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley & Sons, New York, 1956, p. 266.

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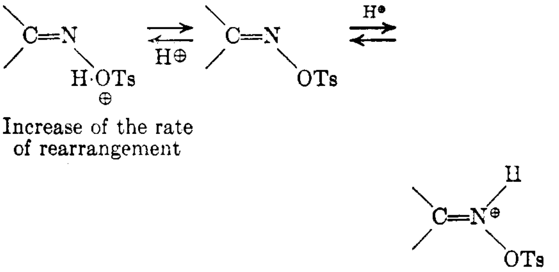
(29) P. T. Scott, D. E. Pearson, and L. J. Bircher, *J. Org. Chem.*, **19**, 1815 (1954).

requires that the exo-double bond of the cycloalkanone oximes in the ground state becomes essentially an endo-double bond in the transition state, which may be represented by C (Equation 8). On the other hand, Huisgen[30] believes that the decisive factor is the change of the coordination number of the α-methylene group from four in the oxime to five in the transition state, *i.e.*, from I to B (Equation 8).

A change of reaction medium changes both the degree of dissociation (Equation 9) and possibly the degree of N.G. participation (Equation 8). A change of the reaction medium from chloroform to acetic acid indicated (see above) that in chloroform, in which presumably only "intimate ion pairs" are present (Equation 9), the transition state for II and IV progressed further toward B (Equation 8) than for I and III. A change of the reaction medium from acetic acid to methanol displaces all compounds but I toward lower $\Delta H^{\ddagger}$ as well as lower $\Delta S^{\ddagger}$ (Fig. 3). This trend may indicate a more rigid, less symmetrical transition state[31] in which bond formation between the solvent may already have taken place, at least for II and IV. Some bond formation with the solvent in the transition state for II is indicated by the relative high value of m (Table VIII). The bond formation can only occur at the C_α and not at the nitrogen of the oxime (Equation 8) since no oxime methyl ethers were ever detected in the methanolysis of oxime *p*-toluenesulfonates.[12] This would indicate that in methanol, and even more so in stronger nucleophilic media, the transition state for II and IV has proceeded still further toward C (Equation 8). On the other hand, a change of the reaction medium from acetic acid to methanol indicates little decrease of $\Delta S^{\ddagger}$ for III and an actual increase of $\Delta S^{\ddagger}$ for I, hence little bond formation between the solvent and the transition state. Addition of small amounts of water to acetic acid likewise did not increase the rate of solvolysis of I (Table I). The study of salt effects in the acetolysis of I indicates the presence of an ion pair return and anion exchange; the ion pair return and anion exchange indicates a relatively stable cation A or B but not C.[3,23] It appears, therefore, that at least with chloroform as the solvent, Huisgen's hypothesis for rearrangement of cyclic oxime *p*-toluenesulfonates is to be preferred.

Acid catalysis. Addition of perchloric acid to the acetolysis of I reduces the rate constant; when 0.085 mequiv. of perchloric acid was added to 0.79 mequiv. of I in 65 ml. of 100% acetic acid, the rate constant decreased by about 20%, *i.e.*, from 6.06 × 10^{-4} sec.$^{-1}$ to 4.49 × 10^{-4} sec.$^{-1}$ Larger increase in the initial concentration of perchloric acid reduces the rate constant of acetolysis still further (Table I). However, addition of 9.2 mequiv. of trifluoroacetic acid to I in chloroform did not decrease the rate constant of rearrangement to any extent. In fact, a large excess of trifluoroacetic acid (83.4 mequiv. to 0.144 mequiv. of I) increased the rate constant from 1.05 × 10^{-4} sec.$^{-1}$ (at 79.8 ± 0.1°) to about 3.8 ± 0.5 × 10^{-4} sec.$^{-1}$ Apparently, the proton may add in two different fashions to the oxime ester depending on the solvent used:



Increase of the rate of rearrangement

Decrease in the rate of rearrangement

In chloroform, the proton adds to the oxygen of the oxime ester accelerating the rate of rearrangement, whereas, in acetic acid, the proton adds to the nitrogen deaccelerating the rearrangement. This rationalization is supported by the isomerization of *syn*-isobutyrophenone oxime to the *anti*-isobutyrophenone oxime in glacial acetic acid as the rearranging agent.[32] Furthermore, the discrimination of an acid for oxygen or nitrogen appears to be a function of kinetic as well as thermodynamic effects.[1d] This is supported by Theilacker, who found that at low temperatures antimony pentachloride adds to the nitrogen of a chlorimine, whereas at higher temperatures, the oxygen complex is formed.[33]

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