

The Effect of Dimethyl Sulfoxide on the Rate of the Wolff-Kishner Reaction of Benzophenone Hydrazone¹

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Abstract: The rate of the Wolff-Kishner reaction of benzophenone hydrazone, in mixtures of butyl carbitol and DMSO and in the temperature range of 100–190°, increases as the concentration of DMSO is increased, but this effect passes through a maximum. The maxima tend to drift toward higher DMSO concentrations as the temperature is lowered. These results are believed to be a manifestation of the hitherto unsuspected dependence of the Wolff-Kishner reaction on the presence and activity of a protic component of the reaction mixture.

The report² that dimethyl sulfoxide (DMSO) produces a spectacular decrease in the temperature requirement of the Wolff-Kishner (WK) reaction, coupled with our long standing interest in the mechanism of this reaction³ as well as in the properties of sulfoxides,⁴ prompted a detailed examination of this pronounced solvent effect. Rather than working in nearly absolute DMSO, we chose to begin this study by examining the effect of the admixture of DMSO to the previously employed hydroxylic solvent, namely butyl carbitol, on the rate of the WK reduction of benzophenone hydrazone.

A previous study³ of the WK reaction of hydrazones in butyl carbitol showed that a minimum temperature of *ca.* 190° was required for a stoichiometric and moderately rapid evolution of nitrogen. The admixture of DMSO to the above-mentioned reaction medium was found to accelerate the rate of the reaction and to give a quantitative evolution of nitrogen at temperatures below 190°. The reaction retained its first-order base dependence irrespective of the concentration of DMSO in the medium, and the sodium alkoxide derived from butyl carbitol was employed as base catalyst. Unexpectedly, however, the effect of DMSO on the reaction velocity reached a maximum past which the rate decreased rather abruptly, and the maxima were displaced toward higher DMSO concentrations as the temperature of the reaction was lowered.

This relationship between the rate constants and the DMSO concentration over the temperature range of 100–195° is summarized in Figure 1.

Experimental Section

The apparatus, experimental procedure, and treatment of the data were the same as previously described³ except that in place of a constant temperature oil bath, the reaction rates were studied in a specially designed reaction flask. The latter consisted of a double-walled cylindrical vessel, the outer part of which contains a steadily refluxing liquid of desired boiling point. The inner chamber, a deep temperature well, is also equipped with a condenser and an outlet for the insertion of the glass capsule containing the sample of the hydrazone. A thermometer placed in the inner chamber provides a direct reading of the temperatures which, upon thermal equilibration, remained constant within $\pm 0.1^\circ$. Thermal equi-

librium was readily attained by the use of a cylindrical heating mantle and insulation of the exposed portions of the apparatus by means of asbestos paper. Since the inner chamber was connected by way of the condenser to a gas buret, the point of thermal equilibration was reflected by the steady behavior of the open arm manometer which forms part of the buret.

The kinetic results are summarized in Table I. It is noted that some of the experiments failed to produce an essentially quantitative evolution of nitrogen. In these experiments the final reaction mixture showed a characteristic deep red color which was discharged (rather slowly) by the addition of water. For these experiments the rate constant was determined by the graphical method assuming a theoretically calculated final volume of nitrogen. The composition of the solvent mixture was determined at room temperature by mixing known volumes of butyl carbitol and DMSO and observing the volume of the resulting mixture. For all practical purposes the volumes of these two components are additive.

The reproducibility of the kinetic experiments can be seen by comparing the results in the following sets of experiments: 17 and 18; 19 and 21; 20, 22, and 28; 23, 24, and 25; 36 and 37; and 92 and 94. The probable error of the rate constants is estimated to be less than 3% of the value. The first-order dependence on base concentration demonstrated in previous work³ holds true also in the presence of DMSO as seen from the results of experiments 22 and 28, or 36 and 37.

Discussion

A possible explanation for the nonlinear relationship between the rate constants and the composition of a binary solvent mixture is that the reaction responds to the change of the dielectric constant of the medium, and that the values of dielectric constant pass through maxima because of association phenomena between the components of the solution. Unfortunately, the dielectric constants of mixtures of DMSO and butyl carbitol are not reported, but we can be guided by the data reported by Lindberg⁵ for the mixtures of DMSO and several other substances. These results are compiled and reproduced in Figure 2, and we note that all mixtures, including that which most closely resembles our case, namely DMSO and 1-butanol, give smooth curves. The data of Lindberg are for binary mixtures at 25° but, off hand, there is no reason to expect that similar smooth curves should not be obtained at higher temperatures at which all the differences between dielectric constants tend to be minimized. Thus, we are led to conclude that the maxima of Figure 1 cannot be explained on the basis of changes in the dielectric constant of the reaction medium. Nevertheless, it is of interest to inquire if there is any evidence that this factor plays a definite role over a more limited range of DMSO

(1) (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; (b) from the M.Sc. Thesis of M. N. R., University of Puerto Rico, 1965.

(2) D. J. Cram, M. R. V. Sahyan, and R. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

(3) H. H. Szmant, *et al.*, *ibid.*, **74**, 2724 (1952); **86**, 2909 (1964).

(4) H. H. Szmant in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, Oxford, 1961.

(5) J. J. Lindberg, *et al.*, *Suomen Kemistilehti*, **B33**, 104 (1960); **B34**, 156 (1961); *Finska Kemistsamfundets Medd.*, **71**, No. 4, 97 (1962).

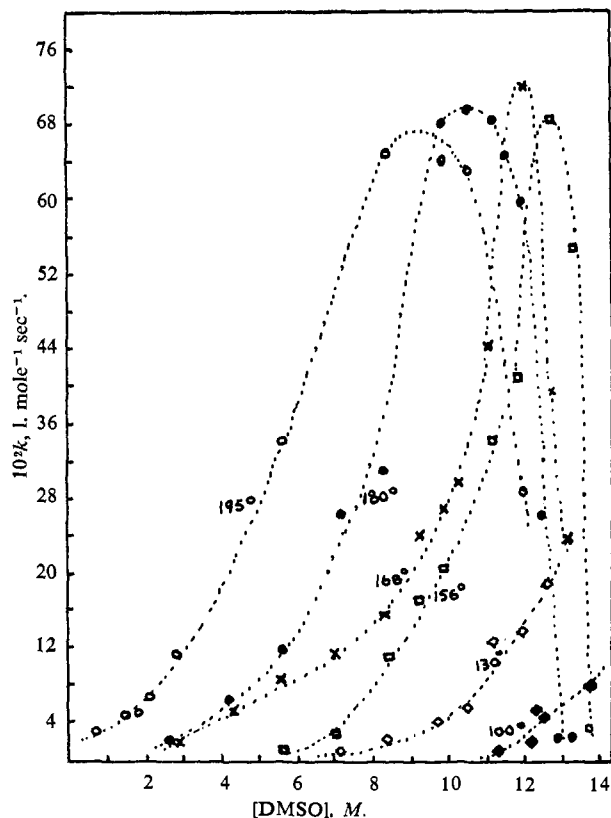


Figure 1. Change in rate constants as a function of [DMSO].

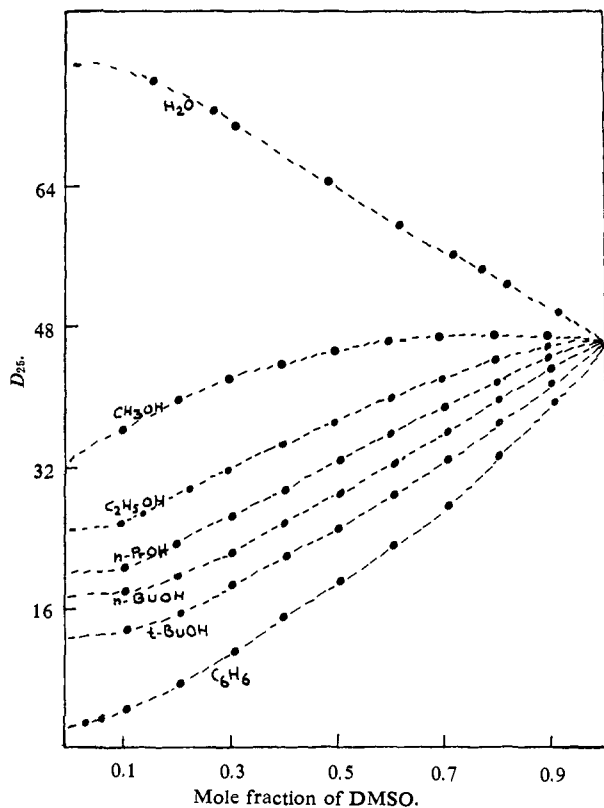


Figure 2. Dielectric constants of binary mixtures of DMSO.

concentrations. For this purpose, the results of Table I are expressed graphically by plotting $\log k$ vs. the mole fraction of DMSO. The trend toward linearity noted (Figure 3) in the lower concentration range of

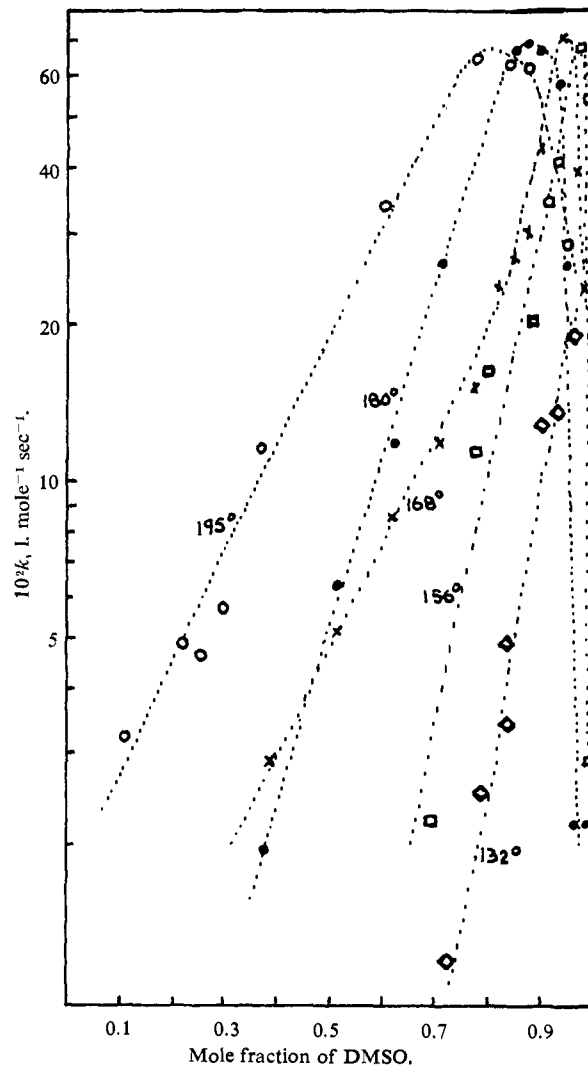


Figure 3. Change in rate constants as a function of [DMSO].

DMSO suggests⁶ that, over this limited concentration range, the catalytic function of DMSO may well result from the increase in the dielectric constant of the medium.

Another explanation of the accelerating effect of DMSO (in the lower range of DMSO concentrations) may be its role in promoting a greater activity of the anion catalyst owing to its well-recognized⁷ ability to solvate the cation of the alkoxide salt, and to associate with the hydroxylic solvent molecules which otherwise deactivate an alkoxide ion through hydrogen bonding. This argument does not seem to be a valid one in our case because, in the first place, there should not be observed a reversal of the accelerating effect of DMSO when its concentration exceeds that at the maxima shown in Figure 1. Also, recent work in this laboratory has shown that the hydrazone anion can be generated in absolute DMSO by means of the dimsyl anion⁸ without an appreciable nitrogen evolution (at room temperature).⁹ Finally, it is known⁷ that the acceleration produced by a change from a hydrogen-bonding to a nonbonding solvent, when an anion participates in a

- (6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 145.
- (7) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).
- (8) J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).
- (9) H. H. Szmant, H. Poussin and C. A. Rivera, unpublished work.

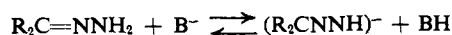
Table I. Summary of Kinetic Experiments^a

Expt no.	Concn ^b of base, <i>M</i>	Final % of theor N ₂	Solvent composition				<i>k</i> × 10 ² , l./mole sec
			DMSO		Bu carbitol		
			<i>M</i>	<i>x</i> ^c	<i>M</i>	<i>x</i> ^c	
195°							
17	0.037	100.0	1.47	0.22	5.37	0.78	4.90
18	0.037	100.0	1.41	0.22	5.37	0.78	4.94
19	0.037	100.0	2.82	0.37	4.72	0.63	11.50
21	0.037	100.0	2.82	0.37	4.72	0.63	11.64
20	0.037	99.5	2.11	0.30	5.01	0.70	5.70
22	0.037	98.0	2.11	0.30	5.01	0.70	5.78
28	0.019	95.8	2.11	0.30	5.01	0.70	5.62
23	0.037	100.0	0.705	0.11	5.60	0.89	3.26
24	0.037	98.6	0.705	0.11	5.60	0.89	3.06
25	0.037	83.3	0.705	0.11	5.60	0.89	3.16
33	0.019	95.8	1.83	0.26	5.12	0.74	4.59
119	0.014	100.0	8.46	0.78	2.36	0.22	65.0
120	0.014	100.0	9.87	0.84	1.76	0.16	63.7
122	0.014	100.0	5.64	0.60	3.82	0.40	34.0
123	0.014	100.0	10.57	0.88	1.49	0.12	62.9
124	0.016	80.1	12.00	0.95	0.57	0.05	28.5
180°							
63	0.020	100.0	7.05	0.71	2.92	0.29	26.5
64	0.020	100.0	5.64	0.62	3.51	0.38	11.8
65	0.034	100.0	4.23	0.51	4.12	0.49	6.44
66	0.034	87.5	2.82	0.38	4.69	0.62	1.97
67	0.034	100.0	11.20	0.90	1.15	0.10	68.43
69	0.020	78.6	13.40	0.98	0.27	0.02	2.19
70	0.020	70.9	12.70	0.95	0.56	0.05	2.19
71	0.020	100.0	12.00	0.94	0.75	0.06	57.9
73	0.020	100.0	12.30	0.945	0.73	0.055	26.5
74	0.026	100.0	8.46	0.79	2.36	0.21	30.4
75	0.012	100.0	10.50	0.87	1.48	0.13	69.6
76	0.012	100.0	11.00	0.89	1.35	0.11	64.0
77	0.012	100.0	9.87	0.85	1.69	0.15	68.3
168°							
59	0.055	100.0	2.82	0.38	4.65	0.62	2.92
60	0.055	100.0	4.23	0.51	4.06	0.49	5.10
61	0.037	100.0	7.05	0.71	2.94	0.29	11.8
62	0.030	98.6	5.64	0.62	3.45	0.38	8.58
78	0.022	100.0	9.87	0.85	1.73	0.15	26.9
81	0.026	100.0	10.57	0.88	1.46	0.12	29.8
82	0.026	98.6	9.16	0.82	2.05	0.18	24.0
85	0.026	98.6	11.20	0.90	1.15	0.10	44.3
86	0.015	100.0	8.46	0.78	2.34	0.22	15.3
89	0.026	95.0	12.70	0.96	0.56	0.04	39.15
91	0.026	98.6	13.40	0.98	0.27	0.02	22.82
136	0.007	98.6	12.00	0.94	0.85	0.06	72.41
15°							
36	0.075	100.0	5.64	0.60	3.70	0.40	0.973
37	0.095	98.6	5.64	0.60	3.73	0.40	0.973
38	0.095	98.6	7.05	0.69	3.14	0.31	2.27
40	0.095	100.0	8.46	0.77	2.55	0.23	11.1
92	0.026	100.0	11.20	0.91	1.15	0.09	34.3
94	0.026	98.6	11.20	0.91	1.15	0.09	34.3
95	0.026	100.0	9.87	0.89	1.34	0.11	20.1
103	0.019	100.0	9.16	0.79	2.35	0.21	17.4
104	0.016	98.6	9.10	0.79	2.35	0.21	17.4
126	0.010	100.0	12.70	0.96	0.68	0.04	68.53
127	0.007	100.0	13.40	0.98	0.28	0.02	54.80
129	0.010	75.0	13.68	0.99	0.17	0.01	2.98
130	0.010	100.0	12.00	0.94	0.76	0.06	41.02
132°							
108	0.019	100.0	8.46	0.78	2.34	0.22	2.57
109	0.019	98.6	11.2	0.89	1.28	0.11	13.0
110	0.019	100.0	9.87	0.84	1.92	0.16	3.41
111	0.019	100.0	7.05	0.71	2.90	0.29	1.23
112	0.019	98.6	12.70	0.96	0.62	0.04	18.75
113	0.019	75.6	12.00	0.93	0.86	0.07	13.69
114	0.019	95.6	10.57	0.86	0.75	0.14	5.16
100°							
140	0.024	100.0	12.65	0.96	0.59	0.045	3.30
141	0.015	100.0	12.39	0.98	0.29	0.021	4.39
143	0.030	100.0	11.26	0.91	1.17	0.094	1.05
144	0.018	100.0	12.24	0.94	0.77	0.059	1.40
145	0.0074	100.0	13.79	0.99	0.12	0.009	7.34

^a The concentration of benzophenone hydrazone was 0.035 *M* in all experiments. ^b The base concentration was examined at the end of each experiment, and those runs were discarded in which a loss greater than 10% of the initial concentration was observed. ^c Mole fractions.

nucleophilic fashion in the rate-limiting step, is of a much greater magnitude than the maximum 10^2 and 10^3 acceleration observed here at the higher and lower temperatures, respectively.

Thus, one is led to conclude that while the first step of the WK reaction is, no doubt, the formation of the hydrazone anion



(where B^- = alkoxide, dimsyl, etc.) the rate-determining step is a reaction of this anion subsequent to its formation.

The experimental results of the present work seem to indicate that the molecules of the hydroxylic solvent form an integral part of the activated complex of the rate-determining step. The shift of the optimum DMSO concentration with temperature strongly suggests the presence of equilibria between the hydroxylic solvent molecules that are "free," or otherwise engaged outside of the activated complex, and those that form a part of the latter. Higher temperatures tend to disrupt the solvation in the activated complex, and thus it is not surprising that the depletion of the hydroxylic solvent manifests itself at an earlier stage. This can be seen by examining (Table II) the temperature dependence of the molar ratio of hydroxylic solvent to hydrazone at the optimum DMSO concentration. Practical limitations of decreasing these ratios are introduced when the base catalyst is provided in the form of an alcohol-alkoxide solution, and this explains why no maxima were observed at 132 and 100°. To circumvent this limitation, work was initiated to determine the rate of the WK reaction in the total absence of hydroxylic solvent by providing the base catalyst in the form of a solution of the dimsyl anion in DMSO,⁸ and under those conditions it is found⁹ that at 100°, for example, the rate constant of 7.34×10^{-2} l./mole sec at 13.79*M* DMSO (Table I) is reduced to 0.1×10^{-2} l./mole sec in absolute DMSO (14.09*M*). Thus we can see that the total exclusion of the hydroxylic solvent causes a considerable decrease in the rate of the WK reaction, and again we must conclude that the hydroxylic solvent plays an important role in the rate-determining step.

Table II. Temperature Dependence of the Molar Ratio of Butyl Carbitol (ROH) to Hydrazone (H) at the Optimum DMSO Concentrations

Temp, °C	DMSO, <i>M</i>	ROH/H
195	9.50	48.6
180	10.70	42.3
168	12.00	25.1
156	12.50	19.4
132	12.70 ^a	17.7
100	13.79 ^a	3.5

^a Upper limit of DMSO concentration employed in this experiment.

This conclusion calls for an explanation of the success² of Cram's conditions for the WK reaction of benzophenone hydrazone at room temperature. The experiment which gave a 90% yield of diphenylmethane consisted of a very slow addition (8-hr period) of 0.010

mole of hydrazone to a solution of DMSO containing 0.0178 mole of potassium *t*-butoxide. It is obvious that any small portion of the hydrazone introduced into such a solution is converted immediately to the hydrazone anion because of the large excess and the high activity of the alkoxide ion. Simultaneously with the ionization of hydrazone, there is liberated an equimolar amount of the alcohol near the hydrazone anion, and therefore the WK reaction can still occur in accord with the requirement postulated above. In recent work⁹ we have simulated the formation of the hydrazone anion (recognized by the characteristic red color and absorption at 540 m μ) by means of the dimsyl anion and found, as mentioned above, that the evolution of nitrogen at room temperature is truly negligible. Even the addition of small amounts of alcohols does little good in promoting the WK reaction (at room temperature). Thus, the liberation of an equimolar amount of the alcohol *within* the solvent cage containing the hydrazone anion seems to be an essential feature of the success of Cram's conditions for the WK reaction. This point is further supported by Cram's observation that under equivalent reaction conditions, except for a faster addition of the hydrazone (30 min), the yield of the WK reaction was decreased to 72% while the formation of benzophenone azine increased from 10 to 22% of theory. This result is taken to mean that the conversion of the hydrazone anion to the next species, on the path of the WK reaction, is slow enough so that the hydrazone anion can also diffuse out of the solvent cage containing the essential hydroxylic component. Once out of the solvent cage, and in the presence of un-ionized hydrazone, the hydrazone anion, an excellent nucleophile, reacts to give the azine. The formation of azine from the hydrazone anion and a hydrazone is analogous to the acid-catalyzed process described previously by Szmant and McGinnis,¹⁰ except that in the latter case the lesser nucleophilic character of the hydrazone is compensated by the greater electrophilic character of the protonated hydrazone. Finally, with respect to Cram's condition for the WK reaction, we must keep in mind that the formation of azine implies the liberation of hydrazine, and we cannot dismiss the possibility that hydrazine functions as the protic participant in the WK reaction.

The above interpretation of Cram's results gains further support from recent work of Grundon and co-workers.¹¹ These investigators find that the WK reaction of benzophenone hydrazone (in the presence of potassium *t*-butoxide) occurs faster and in better yields in toluene than in DMSO (at 100–110°). This observation fits in with the hypothesis that the *t*-butyl alcohol, generated simultaneously with the hydrazone anion, is essential to the WK process. It stands to reason that the probability that the alcohol escapes the solvent cage depends on the affinity between the hydroxylic compound and the surrounding solvent molecules, and the capacity of DMSO to form hydrogen bonds is notoriously greater than that of the π electrons of toluene. Also, the relatively small dielectric constant of toluene favors the coordination by the metallic cation of both the hydrazone anion and the

(10) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **72**, 2890 (1950).

(11) M. F. Grundon, H. B. Henbest, and M. D. Scott, *J. Chem. Soc.*, 1855 (1963).

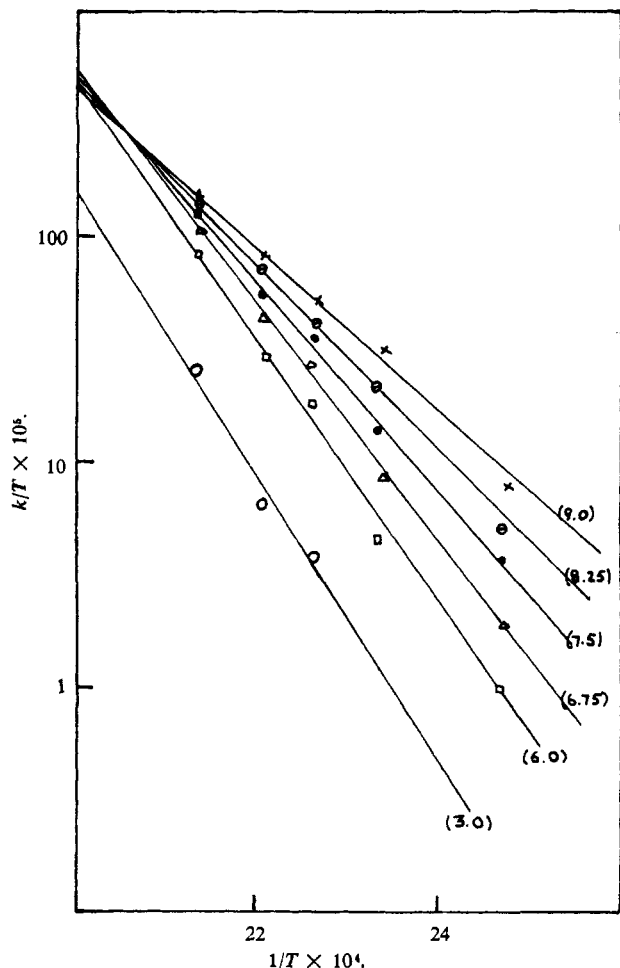


Figure 4. Heats and entropies of activation at different concentrations of DMSO (M).

alcohol, and this also decreases the probability that the alcohol escapes the vicinity of the hydrazone anion. The relatively slow WK reaction in DMSO, even when the hydrazone anion is present together with an equivalent of hydroxylic solvent, fits in with the absence of a kinetic isotope effect when racemization¹² or isotope exchange reactions¹³ are carried out by allowing a hydrocarbon to react with a metal alkoxide in DMSO.

Since the enthalpy and entropy of activation is known³ for the WK reaction of benzophenone hydrazone in a strictly hydroxylic medium, it was of interest to determine the changes in these thermodynamic parameters induced by DMSO. For this purpose the rate constants at different temperatures were read off the curves shown in Figure 1 by intersecting the ascending portions of the curves at different concentrations of DMSO. The application of the Eyring equation to these data gave a family of plots shown in Figure 4 and values of enthalpy and entropy of activation which are summarized in Table III.

The inspection of Figure 4 reveals that, while major shifts in the $\log k/T$ vs. $1/T$ plots are being produced in the lower concentration range of DMSO, the effect of DMSO seems to settle down to a series of gradual changes at approximately 6.75 M , and that, from this

(12) D. J. Cram, C. A. Kingsburg, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

(13) J. E. Hofmann, A. Schriesheim, and R. E. Nickols, *Tetrahedron Letters*, No. 22, 1745 (1965).

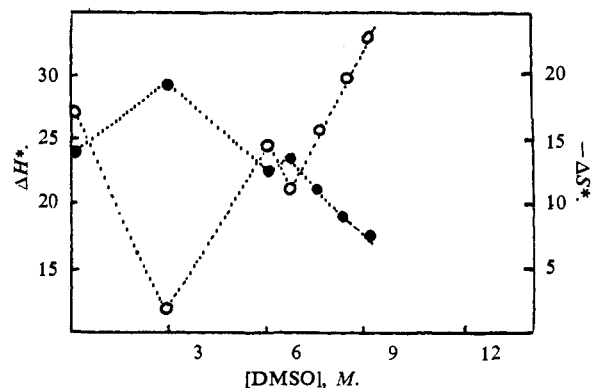


Figure 5. Change in enthalpy (filled circles) and entropy (open circles) of activation as a function of [DMSO].

point on, the decrease in the enthalpy is accompanied by an increase in the negative entropy of activation. This is demonstrated graphically in Figure 5 in which the change in these parameters is plotted as a function of the concentration of DMSO. One is tempted to extrapolate this situation beyond the 9.00 M concentration of DMSO were it not for the fact that the dependence of the reaction upon the concentration of hydroxylic solvent begins to decrease the rates at the higher temperatures. Work now in progress⁹ is designed to fill the gap evident from Figure 5, and especially to determine the thermodynamic parameter of the WK reaction in absolute DMSO.

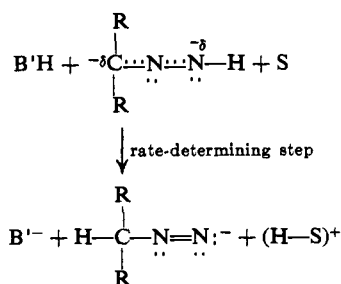
Table III. Enthalpy and Entropy of Activation at Different Concentrations of DMSO

DMSO, M	ΔH^* , kcal/mole	$-\Delta S^*$, eu
9.00	17.6	23
8.25	18.7	20
7.50	21.0	16
6.75	23.6	11
6.00	21.9	15
3.00	29.1	2
0.00	23.6 ^a	17 ^b

If we examine the relative rates of change in the enthalpy and entropy of activation between 6.75 and 9.00 M DMSO (Figure 5) and consider that a tenfold change in reaction velocity is caused by $\Delta\Delta H^*$ of 1.372 kcal/mole or by a $\Delta\Delta S^*$ of 4.6 eu, respectively, we find that the decrease in the enthalpy of activation outweighs the increase in the negative entropy of activation by a factor of 2. Thus, while the effect of DMSO up to a concentration of approximately 6 M seems to center mainly about a favorable increase in the dielectric constant of the reaction medium (note the linear portions of the curves shown in Figure 5), past the concentration of 6.75 M , DMSO apparently begins to participate in collaboration with butyl carbitol in the activated complex, and, by doing so, it lowers the energy of the transition state. It is noteworthy that the latter effect of DMSO becomes discernible when it is present in a twofold molar excess with respect to the hydroxylic solvent.

The above-mentioned observations are compatible with the conclusion reached in the preceding paper of this series³ that the rate-determining step of the Wolff-

Kishner reaction involves a more-or-less concerted formation of a carbon-hydrogen bond and the breaking of the nitrogen-hydrogen bond in the hydrazone anion



where B'-H is a protic solvent such as butyl carbitol, and where S is a hydrogen-acceptor solvent. It is reasonable to expect that DMSO is a superior hydrogen-acceptor solvent than butyl carbitol, and thus we can understand why the presence of DMSO in a mixture of DMSO and alcohol accelerates the WK reaction until the total concentration of the latter becomes so low that it is depleted from the activated complex and the C-H bond formation process begins to suffer. In absolute DMSO at 100° the WK reaction occurs⁹

nearly two magnitudes slower than when a relatively low concentration (0.12 M) of hydroxylic solvent is present, but it is still approximately 30 times faster than the rate calculated from the temperature dependence of the reaction in pure butyl carbitol.⁸ Thus, we may conclude that in absolute DMSO, this normally aprotic solvent is forced into the role of a proton donor¹⁴ and that the reaction rate suffers accordingly, but, in spite of this, the reaction is still faster than in pure butyl carbitol because of the superiority of DMSO, when compared to butyl carbitol, in the role of the hydrogen-bond acceptor.

Since the product of the rate-determining step postulated above is the anion of a diimide,¹⁵ it is to be expected that this anion suffers a rapid elimination of nitrogen, and that the resulting carbanion and the nearby HS⁺ species collapse to the final WK product.

Acknowledgment. We wish to thank Mr. H. Poussin for technical assistance in carrying out some of the experiments.

(14) This point of view will be developed more fully in a future publication.

(15) The first diimide to be studied in detail is that reported recently by E. M. Kosower and P. C. Huang, *J. Am. Chem. Soc.*, **87**, 4645 (1965), and it is shown that the ionization of phenyldiimide under basic conditions is extremely rapid.

Reactions of Epoxides in Dimethyl Sulfoxide Catalyzed by Potassium *t*-Butoxide

Charles C. Price and Donald D. Carmelite¹

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received April 18, 1966

Abstract: The polymerization of ethylene oxide proceeded to completion in DMSO giving a polymer with a molecular weight calculated from the ratio of the monomer to the *t*-butoxide initiator. Propylene oxide gives a polymer with a limiting molecular weight of about 1200, limited by the usual chain-transfer process to the monomer. No detectable sulfoxide end group was observed by infrared in either case, indicating that the methyl hydrogens of propylene oxide are at least 1000 times more readily abstracted by alkoxide groups on growing polymer chains than are hydrogens in DMSO. Substitution of deuterium for the methyl hydrogens of propylene oxide led to an increase in molecular weight and a decrease in allyl unsaturation, as expected for a chain-transfer process involving this methyl group. The reaction of tetramethylethylene oxide with *t*-butoxide in DMSO proceeds solely by attack at methyl, producing α,α,β -trimethylallyl alcohol in 98% yield. Trimethylethylene oxide similarly produces a good yield of two isomeric alcohols, α,α -dimethylallyl alcohol (80%) and α,β -dimethylallyl alcohol (15%). *t*-Butylethylene oxide shows no evidence of chain transfer but is remarkably less reactive to polymerization than propylene oxide.

Earlier studies of epoxide polymerization by strong bases, such as KOH,²⁻⁷ have involved problems of interpretation due to insolubility of the catalyst in the polymerization medium. This has led to the sug-

gestion² that the reaction is heterogeneous for powdered KOH in the monomer or in monomer solutions, although it may only be the initial reaction of KOH with an epoxide to generate a glycolate ion which is indeed heterogeneous.³

Because of the recognition of the value of DMSO solutions of potassium *t*-butoxide for reactions initiated by base,^{8,9} we have now investigated this medium for homogeneous base-catalyzed reactions with epoxides.

For ethylene oxide, polymerization proceeded readily

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