295 mg (1 mmol) of **7** in 30 ml of ethanol was refluxed for 23 hr. Evaporation of the solvent and crystallization of the residue from an ether–ethanol mixture gave 154 mg of a crude mixture of **17a** and **18a** (by nmr). Several recrystallizations from ethanol finally afforded a pure sample (29 mg, 10.3%) of **18a** as yellow prisms, mp 88.5–90.5°, nmr ($CDCl_3$) δ 1.52 (t, 3, CH_3), 4.76 (AB of q, 2, CH_2O), 5.18 (s, 1, H_1), 7.29 (m, 8, ArH), 7.73 (m, 1, H_4).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.49; H, 5.38; N, 5.01.

B.—To a solution of 50 mg (0.18 mmol) of **17a** in 5 ml of methylene chloride was added 1 drop of triethylamine. The solvent was evaporated after 5 min and the crystalline residue was treated with ether and petroleum ether to give 35 mg (70%) of **18a** as yellow prisms, mp and mmp 88–90°.

2-Nitro-1-phenyl-3-methoxyindene (18b). A.—**18b** was similarly prepared (see **18a**, procedure A) in 3.8% yield as yellow prisms, mp and mmp 99–102°, after several recrystallizations from ethanol.

B.—A solution of 5 g (19.75 mmol) of **12** in 100 ml of ether was treated with an excess of ethereal diazomethane solution until no more starting material was present as determined by tlc. Evaporation of the solvent gave an off-white, crystalline solid which on recrystallization from ethyl acetate–ether gave 0.85 g of pale yellow prisms, mp 121–122°, which were identified as 1-phenyl-2-methoxyimino-3-indanone *N*-oxide (**19**), ir ($CHCl_3$) 1700 cm^{-1} (CO), nmr ($CDCl_3$) δ 3.88 (s, 3, CH_3O), 5.07 (s, 1, H_1), 7.0–7.65 (m, 8, ArH), 7.90 (m, 1, H_4).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90: H, 4.90; N, 5.24. Found: C, 72.03; H, 5.11; N, 5.25.

The residual mother liquors and filtrates were combined and evaporated and the residue was chromatographed on 400 g of silica gel using hexane–ethyl acetate (2:1) as the eluent. Removal of solvent from the first fractions, gave an additional 390 mg of **19**, for a combined yield of 1.24 g (23.5%), mp and mmp 121–122°. Later fractions gave, after removal of the solvent, 2.2 g (42%) of **18b** as yellow prisms (crystallized from ethyl acetate–ether), mp 91.5–93°, reset mp 101–102°, nmr ($CDCl_3$) δ 4.37 (s, 3, CH_3O), 5.10 (s, 1, H_1), 6.9–7.45 (m, 8, ArH), 7.70 (m, 1, H_4).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.95; H, 4.94; N, 5.28.

Registry No.—**2,** 34764-52-8; **3,** 34764-53-9; **4,** 34764-54-0; **5,** 34764-55-1; **6,** 34764-56-2; **7,** 34764-57-3; **8,** 34789-54-3; **9a,** 34764-58-4; **9b,** 34764-59-5; **10,** 34764-60-8; **11a,** 34764-61-9; **11b,** 34764-62-0; **12,** 34764-63-1; **14,** 13943-70-9; **16,** 34764-65-3; **17a,** 34764-66-4; **17b,** 34764-67-5; **18a,** 34764-68-6; **18b,** 34764-69-7; **19,** 34764-70-0.

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Thermodynamic and Kinetic Analysis of Meisenheimer Complex Formation

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The free-energy change for the reaction of sodium methoxide with 2,4,6-trinitroanisole (**3**) to give the Meisenheimer complex **2** has been measured and combined with the heat of this reaction to give the entropy change in DMSO–methanol mixtures. Using solubility measurements, the activity coefficients of **3** and the complex **2** have been determined. The free energy, enthalpy, and entropy of transfer of **3** and its complex **2** from pure methanol to methanolic dimethyl sulfoxide solutions have been calculated. The solvent effect on the thermodynamics of the reaction between sodium methoxide and **3** has been measured. The degenerate activity coefficients of sodium methoxide in methanol–DMSO mixtures have been obtained using an indirect method.

The chemistry of Meisenheimer or σ complexes, most of which are substituted cyclohexadienylide ions, has recently come under renewed scrutiny[2] and this research area has been quite active. Dipolar aprotic solvents have been found to enhance the stability of Meisenheimer complexes.[3-8] Indeed, this behavior has made possible the isolation of crystalline sodium and potassium cyclohexadienylides.[3-7] We have demonstrated recently that the increase in the equilibrium constant for the formation of sodium 1,1-dimethoxy-2,4-dicyano-6-nitrocyclohexadienylide (**1**) (eq 1) with increasing DMSO concentration in the DMSO–MeOH solvent system is due to an increase in the rate constant for complex formation (k_1) and a decrease in the rate constant for the decomposition of the complex (k_2).[6] These results have been rationalized using the differences in the hydrogen-bonding power of these solvents. Methoxide ions, being strong hydrogen bond acceptors, become considerably less solvated and, therefore, stronger nucleophiles in dipolar aprotic DMSO than in protic methanol[8,9] Since the 2,4,6-trinitroanisole is not effected strongly by this solvent change, k_1 increases with increasing DMSO concentration. The decrease in the rate constant for the decomposition of the complex (k_2) with increasing DMSO concentration is probably caused by the greater solvation of the highly delocalized negative charge of the complex in

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(1) (a) Texas A & M University; (b) University of Tennessee.

(2) For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution, see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968); (c) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (f) F. Pietra, *Quart. Rev., Chem. Soc.*, **23**, 504 (1969); (g) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(3) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

(4) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *ibid.*, **3**, 4141 (1968).

(5) J. H. Fendler, E. J. Fendler, and C. E. Griffin, *ibid.*, **34**, 689 (1969).

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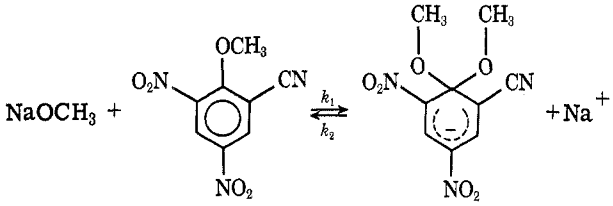
(9) A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 163 (1962); *Advan. Org. Chem.*, **5**, 1 (1965); *Advan. Phys. Org. Chem.*, **5**, 173 (1967); *Chem. Rev.*, **69**, 1 (1969).



(1)

DMSO-rich solvents. These arguments are gross oversimplifications. Any serious consideration of solvent effects on reaction rates must include data on changes in the activity coefficients of the reactants and of the transition state as a function of solvent changes.[10] Even more valuable would be knowledge of the relative enthalpies and entropies of reactants and transition states, and therefore we have undertaken a systematic study of the reaction between 2,4,6-trinitroanisole (**3**) and sodium methoxide in methanol-DMSO mixtures in order to obtain these thermodynamic parameters. We have determined the rate constants for formation (k_1) and decomposition (k_2) of the sodium salt of the complex **2**, as well as measured mean ion activity coefficients of this species, activity coefficients of its parent ether, 2,4,6-trinitroanisole (**3**), heats of formation of the complex **2**, and heats of transfer for both the reactants and the complex. We have combined these data to calculate degenerate activity coefficients for sodium methoxide in methanolic dimethyl sulfoxide.

Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.[3,8,11]

The attainment of the equilibrium for the formation of **2** in methanol and in methanolic DMSO was followed at 495 nm in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The mixing techniques for fast reactions have been described previously.[4] Since the concentration of 2,4,6-trinitroanisole (**3**) was kept at least 20-fold smaller than that of the sodium methoxide, pseudo-first-order kinetics were observed and the corresponding rate constants, k_{obsd}, were calculated from the integrated first-order rate equation.

Rate constants for the decomposition of the complex (k_2) were determined directly by following the absorption decrease at 495 nm of dilute solutions (*ca.* 5×10^{-5} *M*) of solid **2** in the appropriate methanolic DMSO solutions as a function of time. At infinity time the absorption spectra of the solutions were identical with that of **3**.

Six solubility determinations were carried out in each solvent system for **2** and **3**. Three measurements were carried out by shaking solutions containing an excess of the solute at 25.0° and three by shaking saturated solutions at 30° and then cooling to 25.0°. The concentration of the solutes was determined spectrophotometrically. The error in the individual measurements is ±10%. In some cases, the concentration of the saturated solutions of **2** and **3** is greater than 1.0 *M* and thus these solutions are not ideal.

Calorimetric studies were carried out with a dual calorimeter similar to that described by Arnett, Bentrude, Burke, and Duggleby.[8,12] The apparatus was checked at least once a month by measuring the heat of solution of potassium chloride in water. The values obtained agreed within ±1% of the accepted value.[13] The application of these techniques to this system and the purification of reagents have been described previously.[8]

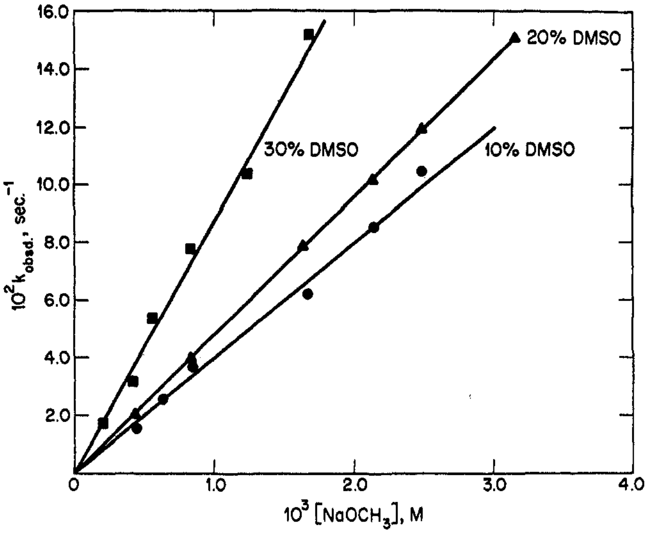
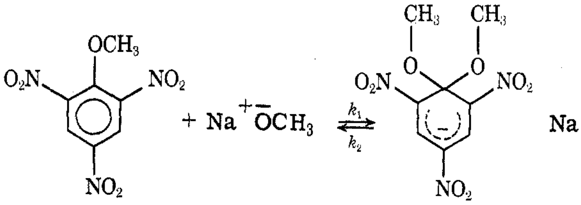


Figure 1.—The dependence of k_{obsd} for the equilibrium attainment of **2** (eq 3) on solvent and sodium methoxide concentration.

Results and Discussion

The addition of a solution of sodium methoxide ([NaOCH$_3$] $> 2 \times 10^{-4}$ *M*) to a solution of 2,4,6-trinitroanisole (*ca.* 10^{-5} *M*) in methanol or in methanolic DMSO results in the formation of complex **2** (eq 2).



3 **2**

(2)

In the methoxide ion concentration range of 2.0–3.0 × 10^{-4} *M* the observed pseudo-first-order rate constant for the equilibrium attainment, k_{obsd}, is given by eq 3,

$$k_{obsd} = k_1[\mathrm{NaOCH_3}] + k_2 \qquad (3)$$

where k_1 is the second-order rate constant for the formation of the complex and k_2 is the first-order rate constant for its decomposition. Figure 1 illustrates the relationship between k_{obsd} and [NaOCH$_3$] according to eq 3. From the slopes of such plots values for k_1 have been obtained and are given in Table I. Values for k_2 are very small, and accurate interpolation from the intercepts of the plots illustrated in Figure 1 is impossible. However, we have obtained k_2 values directly from decomposition of solid **2** in the appropriate methanolic DMSO solution from which the equilibrium constant, $K = k_1/k_2$, can be calculated easily. These data are given in Table I. Also shown in Table I are the heats of the reaction from ref 8 and calculated values for ΔG and ΔS. It must be emphasized that the standard state for these values is dilute solution *in the indicated solvent*. The data in the different solvent systems cannot be compared directly, since each is referred to a different standard state. The data do show how the difference in ΔG or ΔH between the reactants and products (both in the same solvent) is changed as the amount of DMSO in the solvent increases. In the reaction between sodium methoxide and 2,4-dicyano-6-nitroanisole a linear de-

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[10] A. J. Parker and R. Alexander, *J. Amer. Chem. Soc.*, **90**, 3313 (1968); R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968).

[11] We thank Dr. E. J. Fendler for samples of **1**, **2**, and **3**.

[12] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

[13] V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Bureau of Standards, Washington, D. C., Patent NSRDS-NBS2.

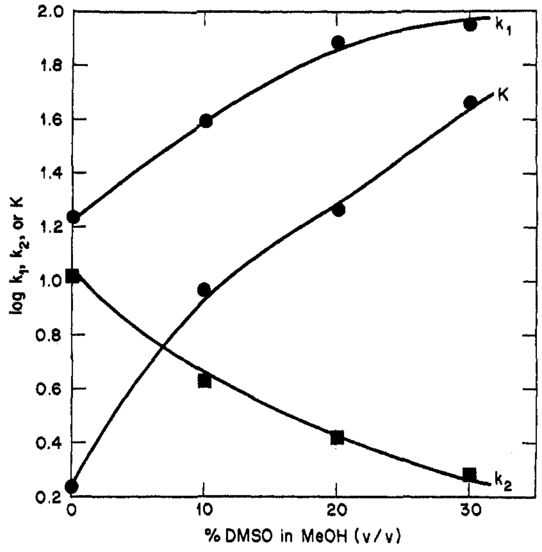

Figure 2.—Solvent effects on the rate constants for formation and decomposition of the Meisenheimer complex **2** and the equilibrium constant for its formation.

TABLE I

EFFECTS OF DIMETHYL SULFOXIDE ON THE KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION AND DECOMPOSITION OF **2** AT 25.0°

	DMSO in MeOH (v/v), %			
	0.00	10.00	20.00	30.00
k_1, M^{-1} sec^{-1} [a]	17.3[b]	39.3	48.0	88.3
10^4k_2, sec^{-1} [c]	10.4[b]	4.25	2.60	1.90
$10^{-4}K$, M^{-1} [d]	1.70[b]	9.26	18.5	46.5
ΔG, kcal/mol[e]	−5.77	−6.77	−7.19	−7.74
ΔH, kcal/mol[e]	−4.86 ±0.03[f]	−6.41 ±0.17	−6.98 ±0.22	−8.47 ±0.26
ΔS, eu[e]	+3.05	+1.21	+0.70	−2.45

[a] Calculated from the slopes of the lines in Figure 1. [b] Determined in ref 5. [c] Determined by decomposing **2** in the appropriate methanolic DMSO. Average of three runs (each within ±3%). [d] Determined from $K = k_1/k_2$ at 25.0°. [e] Thermodynamic parameters on the *equilibrium* for the formation of complex **2**, uncorrected for the activity coefficients of **3** and complex **2**. [f] Recent reestimated value of $-y$ kcal/mol [M. E. C. Biffin, J. Miller, A. Moritz, and D. B. Paul, *Aust. J. Chem.*, **22**, 2561 (1969)] is in good agreement with the experimental value reported here.

pendency of the logarithm of rate and equilibrium constants on the concentration of DMSO (in the DMSO–MeOH system) has been observed.[6] For complex **2** no such linear dependency was observed (Figure 2), illustrating the dangers inherent in attributing mechanistic significance to such plots. A nonlinear dependence of rate and equilibrium constants on solvent composition is not surprising.

To interpret the effects of solvent changes on the kinetics and equilibria of complex formation, the changes in the activity coefficients of the reactants, transition state, and products must be known. The easiest approach to this is to obtain the degenerate activity coefficients for the species involved. We shall adopt dilute solution in methanol as our standard state and determine the activity coefficients relative to this solvent for all the species in the other solvents. By microscopic reversibility, the transition states for the forward and reverse reaction are necessarily identical and are designated by $f'^{\ddagger}$.

Considering the reaction shown in eq 2, the rate constants for the formation of complex **2** in DMSO–MeOH solutions ($k_1^{\mathrm{DMSO-MeOH}}$) are related to the same rate constant in pure methanol by (k_1^{MeOH}) by eq 4.

$$k_1^{\mathrm{DMSO-MeOH}} = k_1^{\mathrm{MeOH}} \frac{f'_{3} f'_{\mathrm{Na^+}} f'_{\mathrm{OCH_3^-}}}{f'^{\ddagger}} \tag{4}$$

Similarly the rate constants for the decomposition of **2** in DMSO–MeOH ($k_2^{\mathrm{DMSO-MeOH}}$) are related to that in pure methanol, k_2^{MeOH}, by eq 5. The degenerate

$$k_2^{\mathrm{DMSO-MeOH}} = k_2^{\mathrm{MeOH}} \frac{f'_{2^-} f'_{\mathrm{Na^+}}}{f'^{\ddagger}} \tag{5}$$

activity coefficients for sodium methoxide are necessary and can be determined in an indirect manner. In essence, since we know K in each of the solvents in addition to the activity coefficients for the reactants and products except for sodium methoxide, we can use these data to get the *relative* activity coefficients (degenerate activity coefficients) for sodium methoxide.

Dividing eq 4 by eq 5 and rearranging gives eq 6.

$$f'_{\mathrm{NaOCH_3}} = \frac{K^{\mathrm{DMSO-MeOH}} \times f'_{2}}{K^{\mathrm{MeOH}} \times f'_{3}} \tag{6}$$

Since all of the quantities in the right-hand side of eq 6 are available, $f'_{\mathrm{NaOCH_3}}$ can be calculated easily. Note that the activity coefficient of sodium methoxide in each solvent ($f_{\mathrm{NaOCH_3}}$) cannot be obtained using this method; only relative values can be obtained. However, this is the additional factor required to determine the effect on changing solvent in the kinetics and thermodynamics of this reaction.

In order to determine the effect of the increasing DMSO concentration on k_1 and k_2, the degenerate activity coefficients for **2**, **3**, and sodium methoxide and that for the transition state are necessary. Degenerate activity coefficients (f') are the activity coefficients for the species in the mixed solvent compared to pure methanol as the standard state ($f'_{2} = f_{2}^{\mathrm{DMSO-MeOH}}/f_{2}^{\mathrm{MeOH}}$, $f'_{3} = f_{3}^{\mathrm{DMSO-MeOH}}/f_{3}^{\mathrm{MeOH}}$, $f'_{\mathrm{NaOCH_3}} = f_{\mathrm{NaOCH_3}}^{\mathrm{DMSO-MeOH}}/f_{\mathrm{NaOH_3}}^{\mathrm{MeOH}}$, and $f'^{\ddagger} = f^{\mathrm{DMSO-MeOH}\ddagger}/f^{\mathrm{MeOH}\ddagger}$). The most convenient way to obtain the necessary activity coefficients is by measuring the solubility of the reactants and product in each solvent, a standard technique.[14] If this is done, then the activity coefficient ratios are given by the solubility ratios; *e.g.*, eq 7, where S is the solubility

$$\frac{f_{\mathrm{x}}^{\mathrm{DMSO-MeOH}}}{f_{\mathrm{x}}^{\mathrm{MeOH}}} = \frac{S_{\mathrm{x}}^{\mathrm{MeOH}}}{S_{\mathrm{x}}^{\mathrm{DMSO-MeOH}}} \tag{7}$$

of species x. Due to the high solubility of sodium methoxide, we were able to obtain data only for 2,4,6-trinitroanisole and the complex **2**. These data are given in Table II. The concentrations are sufficiently high so that the solutions are nonideal; nevertheless, reliable information about the direction and order of magnitude of the solvent effects can unquestionably be obtained from the data.

An independent check of the data in Table II as well as the assumption made in calculating $f'_{\mathrm{NaOCH_3}}$ exists. The degenerate activity coefficient of the transition state $f'^{\ddagger}$ can be calculated using k_1 and the activity coefficients for the starting materials or it can be derived from k_2 and the activity coefficient of the complex. Both values are given in Table II and the agreement is excellent.

The thermodynamic parameters for the reaction in

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(14) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

TABLE II

EFFECTS OF DIMETHYL SULFOXIDE ON THE RELATIVE ACTIVITY COEFFICIENTS OF **2** AND **3** AND ON THE TRANSITION STATES FOR THEIR FORMATION AT 25.0°

	DMSO in MeOH (v/v), %			
	0.00	10.00	20.00	30.00
Solubilities (rel) of **3**[a]	0.184	0.371	0.658	1.085
$f'_{\mathbf{3}}$[b]	1.00	0.495	0.279	0.167
$f'_{\mathrm{NaOCH_3}}$[c]	1.00	4.67	9.18	26.1
$f'^{\ddagger}$[d]	1.00	1.02	0.92	0.85
Solubilities (rel) of **2**[a]	0.730	0.776	3.170	4.672
$f'_{\mathbf{2}}$[e]	1.00	0.414	0.230	0.156
$f'^{\ddagger}$[f]	1.00	1.07	0.920	0.853

[a] Mean of six solubility determinations; see Experimental Section. [b] Degenerate activity coefficients of **3**, $S_3^{\mathrm{MeOH}}/S_3^{\mathrm{DMSO-MeOH}} = f'_3$. [c] Derived from eq 6. [d] Degenerate activity coefficients for the transition state for formation or decomposition of complex **2**. Derived from eq 4 and using $f'_{\mathrm{NaOCH_3}}$ values. [e] Degenerate activity coefficients of **2**; $S_2^{\mathrm{MeOH}}/S_2^{\mathrm{DMSO-MeOH}} = f'_2$. [f] Degenerate activity coefficients for the transition state for formation or decomposition of complex **2** derived from eq 5.

TABLE III

THERMODYNAMICS OF TRANSFER OF THE INDICATED MOLECULES AND THE TRANSITION STATE FROM METHANOL TO METHANOLIC DIMETHYL SULFOXIDE AT 25.0°

	DMSO in MeOH (v/v), %			
	0	10	20	30
2,4,6-Trinitroanisole (**3**)				
ΔG_T,[a] kcal/mol	0	−0.42	−0.76	−1.06
ΔH_T,[b] kcal/mol	0	−0.91	−1.10	−1.24
ΔS_T,[a] eu	0	−1.6	−1.1	−0.60
$NaOCH_3$				
ΔG_T,[a] kcal/mol	0	+0.91	+1.31	+1.93
ΔH_T,[b] kcal/mol	0	+0.6	+1.3	+2.2
ΔS_T,[a] eu	0	−1.0	0	+0.9
Complex **2**				
ΔG_T, kcal/mol	0	−0.52	−0.87	−1.10
ΔH_T,[a] kcal/mol	0	−1.86	−1.92	−2.65
ΔS_T, eu	0	−4.50	−3.52	−5.20
Transition State				
$\Delta G^{\ddagger}$,[b,c] kcal/mol	0	+0.01	−0.05	−0.09

[a] ΔG_T calculated from activity coefficients in Table II; $\Delta S_T = (\Delta H_T - \Delta G_T)/T$. [b] Taken from ref 8. [c] Calculated from $\Delta G_{T,\ \mathrm{complex}\ \mathbf{2}}$ and $\Delta G^{\ddagger}$ from k_2.

TABLE IV

THERMODYNAMICS OF THE REACTION BETWEEN SODIUM METHOXIDE AND 2,4,6-TRINITROANISOLE AT 25.0°

	DMSO, %			
	0	10	20	30
$\delta\Delta G$, kcal/mol[a]	0	−1.01	−1.42	−1.97
$\delta\Delta H$, kcal/mol	0	−1.55	−2.2	−3.61
$\delta\Delta S$, eu	0	−1.9	−2.4	−5.5

[a] Calculated from the data in Table III. See discussion for details.

each of the solvents are given in Table I. In Table IV are these values recalculated using the data from Table III, *i.e.*, correcting the data in Table I for all activity coefficients. The changes are small. There is now enough data to allow examination of the effect of solvent changes on each of the species involved: sodium methoxide, 2,4,6-trinitroanisole, the transition state, and the Meisenheimer complex **2**. Thus we can discover the source of the overall changes in the thermodynamics of the reaction shown in Table I. The necessary relative free energies calculated from the activity coefficients are shown in Table III. The necessary enthalpies of transfer were available from earlier work and the entropies were calculated. It is apparent that the largest change due to varying the solvent is the increase in the free energy of sodium methoxide. The contention that destabilization of sodium methoxide plays an important role in the formation of Meisenheimer complexes is substantiated. The thermodynamics of transfer of sodium methoxide is remarkable in that the variation in entropy is zero within the estimated error; thus $\Delta G_T = \Delta H_T$. This result is surprising, since generally enthalpy changes in a direction opposite to the entropy.[9]

The present thermodynamic data have implications for the derived extrathermodynamic relationship between heats of transfer of sodium and the H_- acidity function.[8] The derived relationship is eq 8. If for

$$H_- = \log \frac{a_{\mathrm{H^+}}\,'a_{\mathrm{Na^+}} f_{\mathrm{MeOH}}}{a_{\mathrm{H^+}} a_{\mathrm{Na^+}}\,'f_{\mathrm{MeOH}}} + \frac{\Delta H_{\mathrm{T,NaOH_3}}}{2.3RT}(1 - T/\beta) \qquad (8)$$

sodium methoxide $\Delta G_T = \Delta H_T$, then β becomes quite large and $(1 - T/\beta) = 1$. Thus the slope of the line of H_- *vs.* $\Delta H_{\mathrm{T,NaOCH_3}}$ should be $1/2.3RT = 1.4$. The observed slope is 1.8.[8] This agreement is good considering the appoximations involved.

The transfer of 2,4,6-trinitroanisole is enthalpy controlled and there apparently exists a minimum in ΔS in the high methanol region. The transfer of the Meisenheimer complex is also enthalpy controlled. In both of these compounds, the entropy and enthalpy are changing in the opposite direction, tending to cancel. Interestingly, the free energy of the transition state is essentially completely insensitive to solvent. It would be nice to know whether this is due to a cancellation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Unfortunately, the data necessary for this analysis are not available.

As shown by the data in Table IV, the overall reaction is enthalpy controlled and the enthalpy and entropy changes are opposed. While the largest contribution is made by the changes in solvation of sodium methoxide, significant changes in the thermodynamic properties of 2,4,6-trinitroanisole and the complex are also occurring and there is no one overwhelming factor dominating the reaction in these solvent systems.

Registry No.—**2**, 12275-58-0; **3**, 606-35-9; dimethyl sulfoxide, 67-68-5.

Acknowledgment.—Support of this work by the Research Corporation (J. W. L.) and the Atomic Energy Commission (J. H. F.) is gratefully acknowledged. The authors are grateful to a referee for his help in developing the thermodynamic analysis used here.