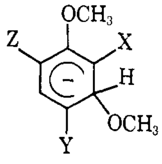
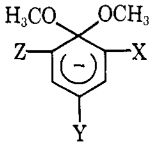
Calorimetric Detection of Transient Intermediates in the Formation of Meisenheimer Complexes

Sir:

The recent renewal of vigorous interest in the chemistry of Meisenheimer complexes[1] has been considerably stimulated by the observation of 2,4,6-trinitro- (I),[2–4] 2-cyano-4,6-dinitro- (II),[5] 4-cyano-2,6-dinitro- (III)[5] and 2,4-dicyano-6-nitro- (IV)[6] substituted 1,3-dimethoxycyclohexadienylide ions in the reaction of the parent aromatic ethers with methoxide ions. I–IV are short-lived species which subsequently convert[7] to the more stable 1,1-dimethoxycyclohexadienylide ions, V–VIII.[2–6] The structures of I–IV have been established from the pmr spectra of the complexes formed *in situ* from the parent aromatic ethers and methanolic potassium methoxide in *DMSO-d_6 solution.* However, due to the relatively short lifetimes of I–IV in methanol in the presence of high concentrations of methoxide ion[8] and the lack of rapid pmr techniques for dilute solutions, species I–IV have not been observed previously in dilute solution in the absence of dimethyl sulfoxide cosolvent. The unavailibility of kinetic and thermodynamic data for Meisenheimer complexes at low concentrations in methanol made the comparison[2] of the calculated thermodynamic parameters of Miller[9] with observations on concentrated solutions in MeOH–DMSO mixtures tenuous.



I, $X = Y = Z = NO_2$
II, $X = CN$; $Y = Z = NO_2$
III, $Y = CN$; $X = Z = NO_2$
IV, $X = Y = CN$; $Z = NO_2$



V, $X = Y = Z = NO_2$
VI, $X = CN$; $Y = Z = NO_2$
VII, $Y = CN$; $X = Z = NO_2$
VIII, $X = Y = CN$; $Z = NO_2$
IX, $X = Z = CN$; $Y = NO_2$

Although calorimetry has been widely applied to organic chemical problems,[10] it has not been significantly utilized previously in the investigation of Meisenheimer complexes. In this communication we report the first observation of a transient species prior to 1,1-complex formation in dilute methanolic solution, in the absence of dipolar aprotic cosolvents, and present thermodynamic parameters obtained by calorimetry for the formation of I and V as well as the observed linear correlations between ΔH and ΔS *vs.* the logarithm of the equilibrium constant for the formation of complexes V–IX.

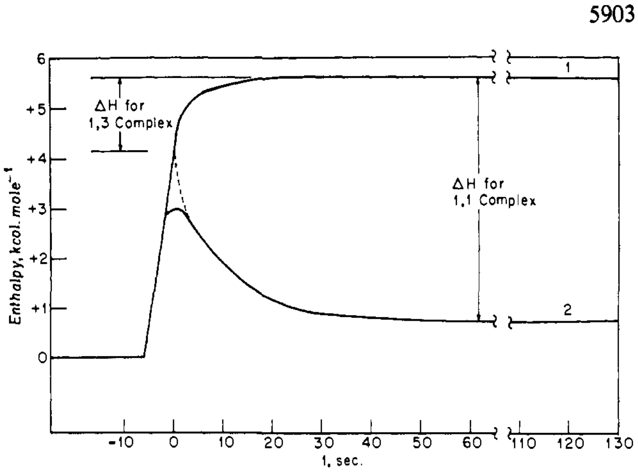


Figure 1. Plots of enthalpy, ΔH, *vs.* time for solid 2,4,6-trinitroanisole in pure methanol (curve 1) and the same quantity of 2,4,6-trinitroanisole in 0.01 *M* methanolic sodium methoxide (curve 2) at 25°.

The response of the calorimeter to the injection of 2,4,6-trinitroanisole into methanol (curve 1) and into methanolic sodium methoxide (curve 2) is shown in Figure 1. Experimentally, a sample of the aromatic starting material is introduced into the calorimeter containing the solvent, and the temperature *vs.* time curve is obtained on a strip chart recorder. Using this and a calibration curve obtained by introducing a known amount of electrical energy the heat of solution can be calculated easily.[10] Repetition of this process using solvent containing methoxide ion yields both the heat of solution of the starting material and the heat of complexation. Simple subtraction then gives the heat of formation of the complex. The curve shown in Figure 1 is a plot of temperature (or ΔH) *vs.* time. Normally, the two curves resulting from dissolution and dissolution accompanied by reaction are identical in appearance but different in magnitude. It is apparent from Figure 1 that a slow exothermic process is occurring. If the exothermic portion of curve 2 is extrapolated until it intersects with the line resulting from the initial endothermic solution process, the maximum falls considerably below the value expected for a simple solution process. Although no structural identification of a transient is possible calorimetrically, it is suggested that the exothermic displacement represents the formation of the 1,3-dimethoxycyclohexadienylide transient. The interaction of methoxide ions with 2,4-dicyano-6-nitroanisole resulted in calorimetric curves similar to those given in Figure 1 indicating the presence of the respective 1,3-dimethoxycyclohexadienylide IV. In contrast, no evidence was obtained for intermediate formation when solid 2,6-dicyano-4-nitroanisole or 1,3,5-trinitrobenzene was injected into solutions containing methoxide ion. These results are in agreement with and substantiate the earlier pmr observation of the importance of a nitro substituent *para* to the site of nu-

[1] For recent reviews 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.* (London), **22**, 123 (1968); P. Buck, *Angew. Chem. Intern. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier Publishing Co., Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

[2] K. L. Servis, *J. Am. Chem. Soc.*, **87**, 5495 (1965); K. L. Servis, *ibid.*, **89**, 1508 (1967).

[3] M. R. Crampton and V. Gold, *J. Chem. Soc.*, *B*, 893 (1966).

[4] R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1966).

[5] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969).

[6] E. J. Fendler, C. E. Griffin, and J. H. Fendler, *Tetrahedron Lett.*, 5631 (1968).

[7] For a discussion of the possible equilibria involved in 1,3- and 1,1-complex formation see footnote 38 in ref 5.

[8] The stabilities of I–IV were found to be inversely proportional to the concentration of methanol present in the methanol–dimethyl sulfoxide solvent system[2,5,6] and the conversion of the 1,3- to the 1,1- complex was found to be catalyzed by methoxide ions.[3,6]

[9] J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963); D. L. Hill, K. C. Ho, and J. Miller, *J. Chem. Soc.*, *B*, 299 (1966).

[10] E. M. Arnett and J. W. Larsen, "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968; E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. C. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

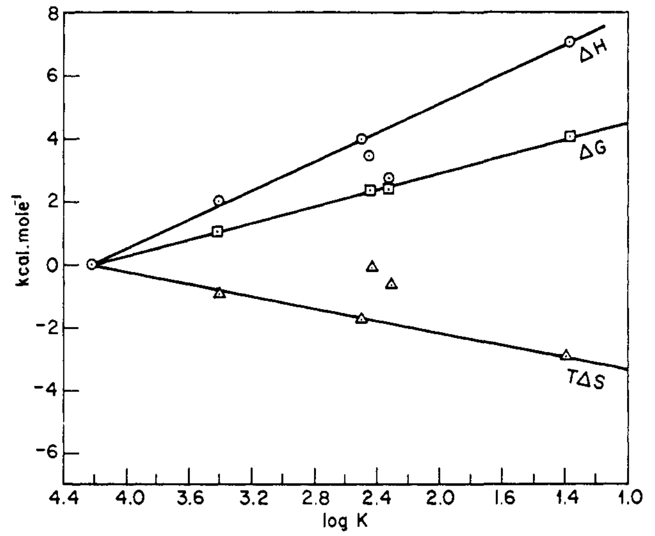


Figure 2. Relative values (to complex V) of ΔG, ΔH, and $T\Delta S$ for Meisenheimer complex formation *vs.* log K for the formation of complexes V–X in methanol at 25°.

cleophilic attack. From the exponential decay of curve 2, the rate constant for the formation of V was calculated to be 10 l. mole^{-1} sec^{-1} at 25°. This value is in reasonable agreement with that obtained by Gold[11] (4 l. mole^{-1} sec^{-1}) under slightly different conditions. The enthalpy of formation of complex I is calculated to be -1.48 ± 0.5 kcal/mole, assuming that the equilibrium constant for its formation is greater than 10^3. The concentration independence of the enthalpy of formation substantiates this assumption.

The free energies, enthalpies, and entropies of formation for complexes V–IX and 1-methoxy-2,4,6-trinitrocylohexadienylide ion (X) are given in Table I.[12] Linear relationships have been found between ΔH, ΔS, and log K as shown in Figure 2. The substituent effects on the enthalpy and entropy of complex formation are large and in opposing directions, resulting, of course, in smaller changes in the free energy. The extent of this type of linear correlation in Meisenheimer complex formation as well as the effects of solvents on the different thermodynamic parameters are under investigation in our laboratories.

Table I. Thermodynamics of Meisenheimer Complex Formation at 25°[a]

Complex	ΔG,[b] kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, eu
V	-5.77	-4.86 ± 0.03[c]	$+3.0$
VI	-4.66	-2.82 ± 0.47	$+6.2$
VII	-3.29	-3.41 ± 0.28	-0.40
VIII	-1.36		
VIII[d]	-3.4[e]	-0.82 ± 0.49	$+8.7$
IX	-2.09	Endothermic	
IX[f]	-3.2	-2.23 ± 0.55	$+3.3$
X	-1.6	$+2.15 \pm 0.82$	$+12.6$

[a] In methanol unless stated otherwise. [b] Obtained from spectrophotometric equilibrium constant measurements.[13] [c] The difference between this value and that determined earlier (J. H. Fendler, *J. Am. Chem. Soc.*, **88**, 1237 (1966)) is a reflection of the more precise experimental technique used in the present work. [d] In DMSO–MeOH, 15:85 (v/v). [e] Based on a value of K calculated by the method of T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965). [f] In DMSO–MeOH, 20:80 (v/v).

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(11) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964).

(12) The concentrations of the reactants were kept below 0.013 M and the heats of formation were calculated by subtracting the heat of solution of the solid aromatic ether in the appropriate solvent from the heat of solution and reaction in the same solvent containing sodium methoxide. Since the enthalpy of complex formation was calculated using values of K,[6,13] the accuracy of the H values depend on the errors in K.

(13) E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larsen, to be published.

A Novel Effect of Carbon Dioxide on Catalyst Properties. Dimerization of Butadiene

Sir:

While studying the dimerization of butadiene in the presence of nickel, palladium, and platinum complexes, we discovered that carbon dioxide can profoundly alter catalyst properties (see Table I). In the absence of a catalyst, butadiene of course slowly dimerizes to 4-vinyl-1-cyclohexene. This uncatalyzed reaction is not altered by including nitrogen, argon, or carbon dioxide under pressure in the autoclave (expt 1 and 4). With $(Ph_3P)_3Pt$[1] present, the product is still 90–97% 4-vinyl-1-cyclohexene, along with a small amount of 1,3,7-octatriene, provided the autoclave atmosphere is either nitrogen or argon (expt 2, 5, and 7). However, with carbon dioxide present, $(Ph_3P)_3Pt$ converts butadiene mainly to *trans*-1,3,7-octatriene[2] (expt 3, 6, and 8). Catalyst activity is significantly enhanced since the conversions of butadiene are greater when carbon dioxide is present (compare expt 2 and 3, 5 and 6, 7 and 8). The effect of carbon dioxide on the product composition is more pronounced at 95° than at 120° presumably because the competitive thermal dimerization is less favored at the lower temperature (compare expt 7 and 8 with 2 and 3).

Oxygen must be carefully excluded from the system, otherwise the product is mainly 4-vinyl-1-cyclohexene; *cf.* expt 3 with expt 9 where air was deliberately introduced. Probably, with oxygen and carbon dioxide both

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(1) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); L. Malatesta and R. Ugo, *ibid.*, 2080 (1963).

(2) A detailed structure proof of this material will be published separately by Dr. E. J. Smutny and coworkers. The *trans* isomer content of the triene was >96% as determined by infrared spectroscopy. For a preliminary report on 1,3,7-octatriene see E. J. Smutny, *J. Am. Chem. Soc.*, **89**, 6793 (1967).