Kinetic Studies of the Formation and Decomposition of the Meisenheimer Complex of 2, 4, 6-Trinitroanisole with Sodium Methoxide in Methanol

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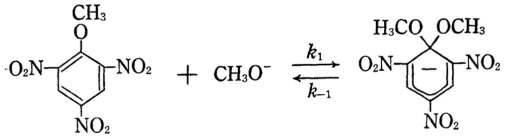
It has been widely accepted that aromatic polynitro-compounds react with alkalis to form colored intermediates of Meisenheimer's type. However, no investigation of the kinetics of both the coloration and the decoloration reactions has hitherto been reported on the color reaction of a polynitrobenzene in an alkaline solvent, although there have been several papers reporting the activation energy for either the coloration or the decoloration. In the present work, therefore, an attempt has been made to obtain the activation energies for the formation and decomposition of the Meisenheimer complex of 2, 4, 6-trinitroanisole with sodium methoxide in methanol.

It has been reported that 2, 4, 6-trinitroanisole reacts with the methoxide ion as follows:[1-9)]



(1)

The Meisenheimer complex

The Meisenheimer complex in methanol has two absorption maxima, at about 485 and 415 mμ.[8,9)]

Experimental

Materials. — Commercial-grade 2, 4, 6-trinitroanisole was purified by several recrystallizations from methanol to a constant melting point. The Meisenheimer complex used was prepared by the same method as in the previous paper.[8)] A solution of sodium methoxide in methanol was prepared by mixing freshly-cut pieces of sodium in methanol. The concentration was determined by the titration of samples diluted with water against a standard aqueous solution of hydrochloric acid. Methanol of a commercial grade was used without further purification.

Measurements.—Each run of the decomposition of the Meisenheimer complex prepared was started by the dissolution of very small pieces of the complex in methanol at the temperature of the thermostat. The rate of decomposition was followed by measuring the absorbancy at 480 mμ.

Each run of the formation of the Meisenheimer complex was started by pipetting 1 ml. of the methanolic sodium methoxide solution (2.025×10^{-3} M) into 2 ml. of the methanolic solution of 2, 4, 6-trinitroanisole (3.980×10^{-5} M) in a cell at the temperature of the thermostat. The resulting solution was then stirred by bubbles of nitrogen gas. The change in the absorbancy at 410 mμ was followed.

In the wavelength region above 400 mμ, 2, 4, 6-trinitroanisole scarcely absorbs at the low concentration of 2.65×10^{-5} M, but it does at higher concentrations. The Meisenheimer complex absorbs more intensely at 410 mμ than at 480 mu. Moreover, it is likely that, at high concentrations of the methoxide ion, 2, 4, 6-trinitroanisole further reacts with the methoxide ion to form a second complex,[9)] possibly absorbing in the visible region. (Details of this will be published later.) Accordingly, the absorbances at 410 mμ were measured for the runs of the formation of the Meisenheimer complex. The methoxide ion does not absorb in this wavelength range. On the other hand, the Meisenheimer complex slowly dissolves and rapidly decomposes in methanol. For convenience, therefore, the colored solutions for the runs of the decomposition were prepared by dissolving the Meisenheimer complex in methanol at arbitrary concentrations. The solutions contained considerable amounts of 2, 4, 6-trinitroanisole which results from the decomposition of the Meisenheimer complex. Consequently, the runs for the decomposition were followed by measuring the absorbancy at the longer wavelength of 480 mμ, at which scarcely any 2, 4, 6-trinitroanisole absorbs at high concentrations.

The absorbancies were measured with a Hitachi EPU-2A quartz spectrophotometer, a pair of 1 cm. cells with ground glass-stoppers being used in a thermostatted cell housing at constant temperatures. The temperature control in all cases was better than ±0.1°C. Methanol was used as a blank.

Results

The Decomposition of the Meisenheimer Complex.—The decomposition of the Meisenheimer complex in methanol obeyed the first-order equation:

$$-\log A=(t-t_0)k_{-1}/2.303-\log A_0 \qquad (2)$$

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1) J. Meisenheimer, *Ann. Phys. Lpz.*, **323**, 205 (1902).
2) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
3) R. Foster, *Nature*, **183**, 1042 (1959).
4) R. C. Farmer, *J. Chem. Soc.*, **1959**, 3425.
5) L. K. Dyall, ibid., **1960**, 5160.
6) S. Nagakura, *Tetrahedron*, **19**, 361 (1963).
7) J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).
8) T. Abe, This Bulletin, **37**, 508 (1964).
9) V. Gold and C. H. Rochester, *J. Chem. Soc.*, **1964**, 1687.

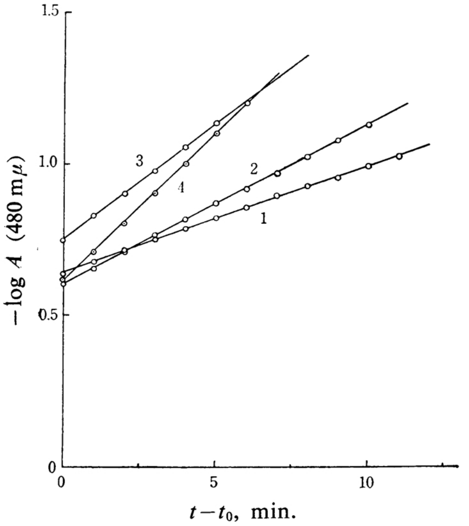

Fig. 1. Rates of decoloration reaction of the Meisenheimer complex in methanol.
1: 20.0°C 2: 25.0°C
3: 30.0°C 4: 34.0°C

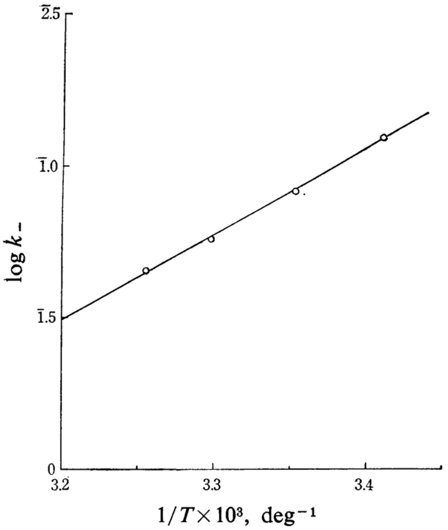

Fig. 2. Plots of $\log k_{-1}$ against reciprocal absolute temperature $1/T$°K.

Here A is the absorbancy of the solution measured at time t, and the subscript zero indicates the starting time. By the least-squares calculations for the observed values in Fig. 1, we obtained the rate constants, k_{-1}'s, from whose temperature dependency in Fig. 2 the activation energy, E_{-1}, was found to be 12.9 kcal./mol.

The Formation of the Meisenheimer Complex.—The result of the runs for the reaction between 2, 4, 6-trinitroanisole and sodium methoxide are shown in Fig. 3. It is obvious from the figure that the reaction is exothermic,

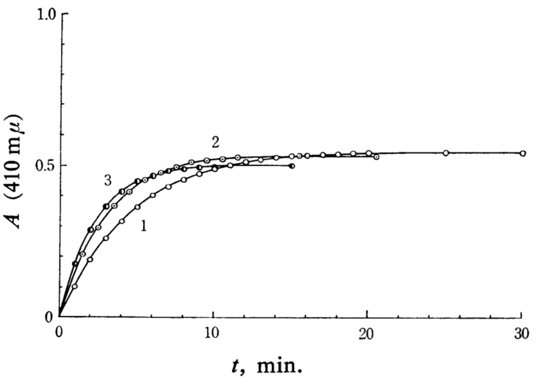

Fig. 3. Rates of reaction of 2, 4, 6-trinitroanisole (2.653×10^{-5} M) with sodium methoxide (6.75×10^{-4} M) in methanol.
1: 20.0°C 2: 25.0°C 3: 30.0°C

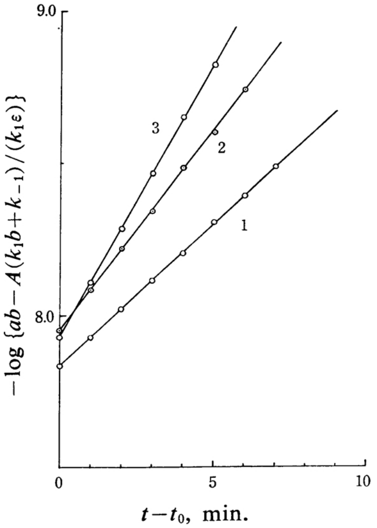

Fig. 4. Plots of $-\log\{ab-A(k_1b+k_{-1})/(k_1\varepsilon)\}$ against $(t-t_0)$.
1: 20.0°C, $(k_1b+k_{-1})/(k_1\varepsilon)=3.23\times10^{-8}$ mol./l.
2: 25.0°C, $(k_1b+k_{-1})/(k_1\varepsilon)=3.24\times10^{-8}$ mol./l.
3: 30.0°C, $(k_1b+k_{-1})/(k_1\varepsilon)=3.50\times10^{-8}$ mol./l.

because the absorbancy at the equilibrium point becomes lower as the temperature increases. If the initial concentration of 2, 4, 6-trinitroanisole (a) is considerably smaller than that of sodium methoxide ion (b), reaction mechanism 1 gives the kinetic equation of the second order as:

$$t-t_0=2.303\,[\log\{ab-A_0(k_1b+k_{-1})/(k_1\varepsilon)\}-\log\{ab-A(k_1b+k_{-1})/(k_1\varepsilon)\}]/(k_1b+k_{-1}) \quad (3)$$

where k_1 is the rate constant of the forward reaction, and ε is the molar extinction coefficient of the Meisenheimer complex. By the trial-and-error method we found the values of

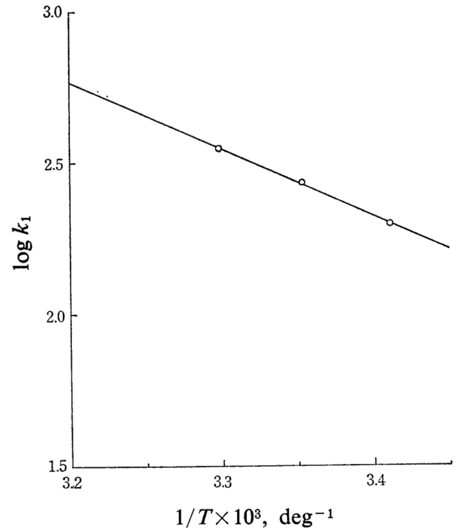

Fig. 5. Plots of k_1 against reciprocal absolute temperature $1/T$°K.

$(k_1b+k_{-1})/(k_1\varepsilon)$ that gave the best straight lines for the plots of $-\log\{ab-A(k_1b+k_{-1})/(k_1\varepsilon)\}$ against $(t-t_0)$ to be those shown in Fig. 4. From the slopes of the plots the values of k_1 were determined to be those listed in Table I, where the values of k_{-1} determined above were used. The activation energy, E_1, obtained from Fig. 5 is 10.1 kcal./mol. The equilibrium constants k_1's, for equilibrium 1 were estimated from the values of k_1/k_{-1}. The values of ε in Table I were estimated from $(k_1b+k_{-1})/(k_1\varepsilon)$.

TABLE I. RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE REACTION OF 2,4,6-TRINITROANISOLE WITH METHOXIDE ION IN METHANOL

Temp. °C	k_1 l./mol. min.	$10k_{-1}$ min^{-1}	K_1 l./mol.	$10^{-4}\varepsilon$ 410 mμ
20.0	200	0.814	2450	3.35
25.0	273	1.21	2260	3.45
30.0	354	1.74	2030	3.34
34.0	—	2.23	—	—

Discussion

It is evident from Fig. 6 that the Meisenheimer complex of 2, 4, 6-trinitroanisole is quite stable. This leads to the interpretation of why the complex is easily prepared.

Assuming that 2, 4, 6-trinitroanisole at 3.43×10^{-5} M was completely converted into the Meisenheimer complex at the methoxide concentration of 1.28×10^{-1} M, Gold and Rochester[9] obtained the value of 7.7×10^3 l./mol. for k_1 at 25°C and the value of 2.42×10^4 for ε at 410 mμ. This K_1 value is much higher than the present one of 2.26×10^3 l./mol. They estimated the rough values of 240 l./mol. min. and 3×10^{-2}/min. for k_1 and k_{-1} respectively at 25°C.

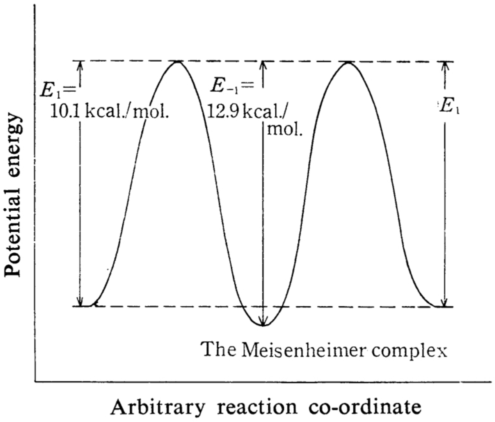

Fig. 6. The energy profile for the reaction of 2, 4, 6-trinitroanisole with sodium methoxide in methanol.

Our activation energy of 10.1 kcal./mol. for the forward reaction corresponds to Ainscough and Caldin's value of 13.1 kcal./mol. for the "slow" reaction of 2, 4, 6-trinitroanisole with ethanolic sodium ethoxide at temperatures from −20° to 10°C.[2]

Miller[7] calculated the activation energies for the same reaction, utilizing bond energies, electron affinities and solvation energies. According to his calculation, the values of E_1 and E_{-1} are 14 and 16 kcal./mol., respectively; these values accord fairly well with our experimental values. By means of the simple LCAO MO method, Abe[8] also made the same calculation, although he did not consider the important solvation energy. His value of 15.7 kcal./mol., for E_{-1} is, however, fairly good. This seems to be due to the cancellation of the solvation energies for a σ- and a π-part in his calculation.

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