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KINETIC STUDY ON ANIONIC σ-COMPLEX FORMATION BETWEEN 2,4,6-TRINITROANISOLE AND METHOXIDE ION BY HIGH PRESSURE STOPPED-FLOW METHOD

Noboru TAKISAWA, Muneo SASAKI, Fujitsugu AMITA, and Jiro OSUGI
Department of Chemistry, Faculty of Science,
Kyoto University, Kitashirakawa Oiwake-cho, Kyoto 606

The high pressure stopped-flow apparatus has been developed which enables to follow reaction rates three seconds after mixing up to 1500 bar. The activation volume at 25°C for the Meisenheimer complex formation between 2,4,6-trinitroanisole and methoxide ion in methanol was determined to be -7.2 ± 0.8 cm^3mol^{-1}.

The effect of pressure on the Meisenheimer complex formation has not been studied nevertheless this is a typical anionic σ-complex formation accompanying the charge delocalization from anionic base to aromatic ring.1) This type of reaction is usually so fast that it is difficult to follow the reaction rate by the conventional high pressure technique. The development of the High Pressure Stopped-Flow (HPSF) method has long been awaited. In 1977 Heremans *et al.* designed the apparatus2) capable of measuring a rate of reaction at pressures up to 1200 bar (1 bar=10^5 Pa) by putting a stopped-flow unit of syringe-driving type into a high pressure bomb. Here, we will describe the construction of a HPSF apparatus different from Heremans and his coworkers' and the results of the pressure effect on the Meisenheimer complex formation between 2,4,6-trinitroanisole (TNA) and methoxide ion.

The schematic diagram of HPSF instrument is given in Fig.1. The high pressure optical cell (HPOC) which contains a mixing chamber and is equipped with two quartz or sapphire windows is shown in Fig.2. The spectrophotometric system was that of Union

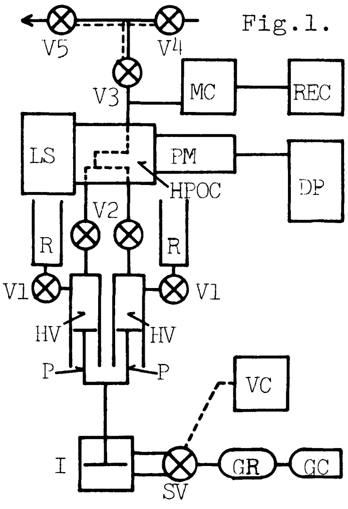


Fig.1. Schematic diagram of HPSF apparatus. GC-Gas cylinder; GR-Gas reservoir; I-Intensifier; P-Piston; HV-High pressure vessel; R-Reservoir; V1∿V5-Valve; VC-Valve controller; SV-Solenoid valve; LS-Light source; HPOC-High pressure optical cell; MC-Manganin coil cell; REC-Recorder; PM-Photomultiplier; DP-Data processor.

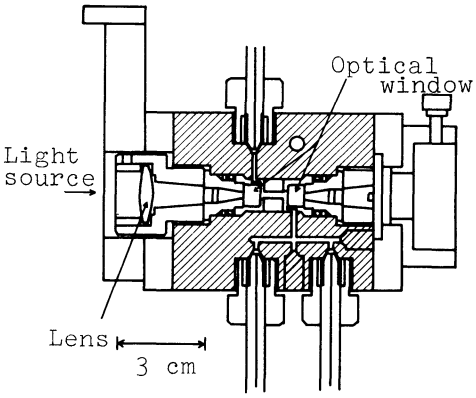


Fig.2. High pressure optical cell and mixing room.

Giken stopped-flow apparatus. Pressure was measured by a manganin coil which was corrected for a Heise bourdon gage with the error of ±10 bar. The mixing was made by a simple T-jet type, and the optical path length was about 10 mm (Fig.2). The temperature was kept at 25±0.5°C by circulating the thermostated water around solution reservoirs R, HPOC, and the connected tubes.

The operation has been carried out as follows (refer to Fig.1). (i) After filling the high pressure system with reactant solutions, the valves V1 and V3 are closed and the valves V2 are opened. (ii) The solenoid valve SV is opened so as to push the piston P upward through the intensifier I by constant gaseous pressure of 1∿7 bar till the desired pressure is generated. (iii) The solutions being kept pressurized, they are flowed by either of following two methods: (a) The valve V3 is opened for a moment. (b) The space indicated by ═══ in Fig.1 is emptied by a water-jet pump and the valves V4 and V5 are closed. Then the valve V3 is opened.

The fluctuation of pressure during these operations is shown in Fig.3. At the point A, V3 is momentarily opened and so the pistons P rapidly put the new solution from the high pressure vessel HV to HPOC. The pressure decreases first to the point B and then is partly recovered to the point C. The rapid recovery of pressure cannot be achieved because of slow movement of the pistons P due to the friction of O-rings used in P and I. (iv) The valves V2 are closed as soon as the operation (iii) has been done (the point C), otherwise pressure goes up slowly from the point C to D, and the solutions result in the inefficient mixing. With this operation the pressure drop by *ca.* 40 bar occurred and it was unavoidable in this apparatus. The reliable kinetic data may be obtained three seconds after the point A.

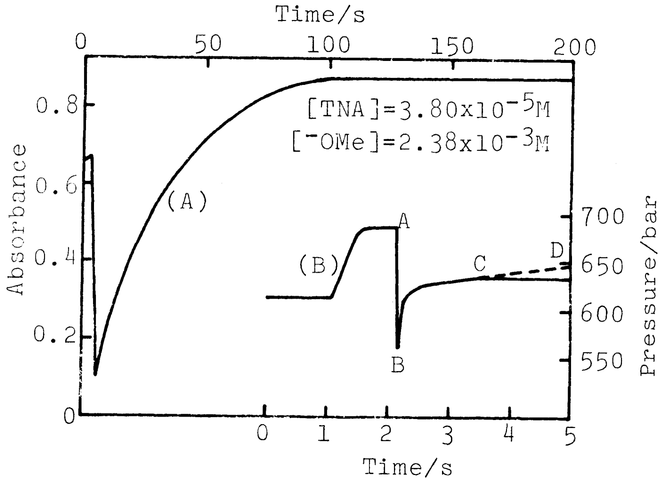
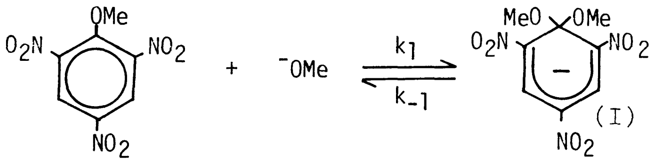


Fig.3. Changes of absorbance (A) and pressure (B) with time.

The efficiency of this apparatus was tested by the Meisenheimer complex formation between TNA and sodium methoxide in methanol. The pseudo first-order plot gave a good straight line within the error of ±0.5% and neither residual solution nor delayed flow was recognized. The reproducibility of the pseudo first-order rate constant was within ±5%. The error may be caused by the uncertainty of the mixing ratio due to the manual operation of V2 to prevent the delayed flow. In this instrument, the repeated measurement was very easy. By a full stroke of the pistons P, five experimental runs were possible, and new solution was easily charged again from R into HV by operating valves V1, V2, and SV.

Trinitroanisole reacts on methoxide ion in methanol to give the Meisenheimer complex (I) having two absorption maxima at 410 and 480 nm [equation (1)]. Under the experimental



(1)

conditions, [TNA]<<[$^{-}$OMe], a pseudo first-order rate constant for equilibrium attainment, k_{obs}, is expressed by equation (2).

$$k_{obs} = k_1[^{-}\mathrm{OMe}] + k_{-1} \qquad (2)$$

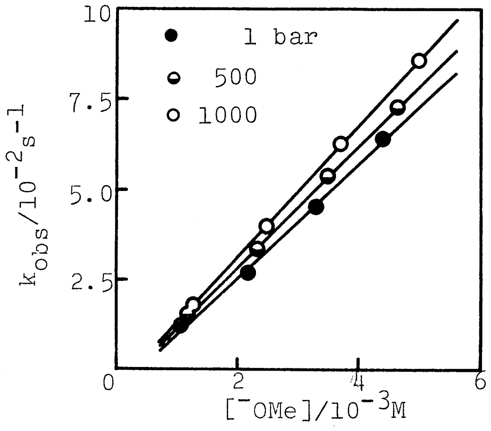


Fig.4. Dependence of k_{obs} on [$^{-}$OMe] in methanol at 25°C.

The dependences of k_{obs}, which was measured from the time dependence of the absorbance at 410 nm by HPSF method, on the methoxide concentration at several pressures are given in Fig.4. From the slopes of such plots the value of k_1 at each pressure is obtained as given in Table 1. Since the intercepts of such plots had slightly negative values, k_{obs} was measured again at constant ionic strength which was controlled by sodium perchlorate to check if there exist the influence of the ionic strength and ion pair formation between the complex (I) and sodium ion. But any meaningful difference has not been recognized. Finally the negateve intercept appears probably due to a large error of k_{obs} (±5%) and very small value of k_{-1} compared with that of k_1 (k_1/k_{-1} $=1.7\times10^4$ at atmospheric pressure[3]). So it seemed impossible to determine the values of k_{-1} unless the decomposition of (I) was followed directly.

Table 1. Pressure dependence of k_1

P/bar	1	250	500	750	1000
$k_1/s^{-1}M^{-1}$	15.4	16.2	16.8	17.4	18.1

Then, from the values of k_1 at several pressures the activation volume of complex (I) formation was determined based on equation (3), where $RT\Sigma\nu_1^{\ddagger}\kappa$ is the term intro-

$$\left(\frac{RT\partial\ln k_1}{\partial P}\right)_T = -\Delta V_1^{\ddagger} + RT\Sigma\nu_1^{\ddagger}\kappa \qquad (3)$$

duced by the use of molarity, $\Sigma\nu_1^{\ddagger}$ the difference of the number of molecules between the initial state and the transition state, and κ the compressibility of the solvent. In methanol, the term $RT\kappa$ is equal to 3.2 $cm^3\cdot mol^{-1}$ at 25°C.[4] The plot of $RT\ln k_1$ *vs.* pressure is given in Fig.5, and from the slope of this plot the activation volume for complex (I) formation, $\Delta V_1^{\ddagger}$, has been calculated to be -7.2 ± 0.8 cm^3mol^{-1}. Generally, the activation volume $\Delta V^{\ddagger}$, as well as the volume change, ΔV, for a reaction can be discussed from the point of view that it consists of two terms; the structure term, $(\Delta V^{\ddagger})_{str}$, and the solvation term, $(\Delta V^{\ddagger})_{solv}$. In this case the structure of complex (I) is already known from the X-ray diffraction,[5] so $(\Delta V_1^{\ddagger})_{str}$ for complex (I) formation has been estimated to be -5.6 $cm^3\cdot mol^{-1}$ from the simple cylindrical model using the assumption that only one C-O bond-length

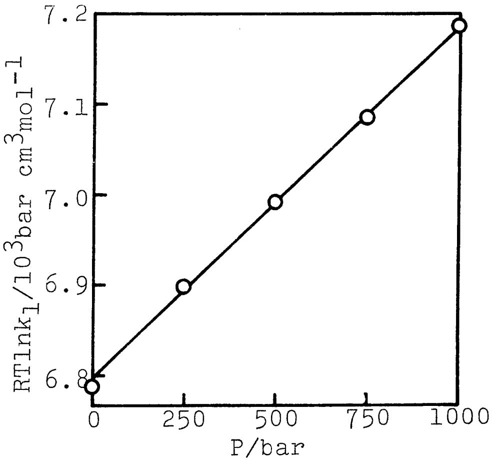
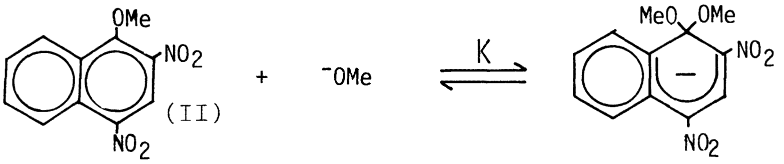


Fig.5. Pressure dependence of $RT\ln k_1$ of complex (I) formation.

between the ring carbon and the methoxy group increases by 30%$^{6)}$ at the transition state as compared with that of (I). Since little difference appears between $(\Delta V_1^{\ddagger})_{str}$ and $\Delta V_1^{\ddagger}$, the solvation term, $(\Delta V_1^{\ddagger})_{solv}$ is considered to be small. So it is suggested that the degree of the solvation of transition state is similar to that of methoxide ion. Accordingly at the transition state, the negative charge of the attacking methoxide ion may be either still localized at the methoxide group or localized at 4-NO_2 group as well as complex (I). In the former, the transition state may be reactantlike and in the latter productlike. But at present, it is uncertain which is the case.

The comparison of $\Delta V^{\ddagger}$ with volume change ΔV is expected so as to elucidate the volume profile during the course of the reaction. However, the determination of ΔV for reaction (1) was impossible as the equilibrium constant was too large. So, the authors chose another system similar to reaction (1), that is, the anionic σ-complex formation between 1-methoxy-2,4-dinitronaphthalene (II) and methoxide ion [equation (4)]. From the pressure effect on the equilibrium constant K by spectrophotometric



(4)

method, ΔV for reaction (4) was found to be -5.2 ± 1.3 cm^3mol^{-1}.

Based on the assumption that the volume change of reaction (4) is similar to that of reaction (1), it may be said that $\Delta V_1^{\ddagger}$ for reaction (1) is colse to ΔV. Namely, from the volumetrical point of view, the transition state is suggested to be like the product.

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