CHEMISTRY LETTERS, pp. 1289-1292, 1976. Published by the Chemical Society of Japan

HIGH PRESSURE CELLS FOR THE STUDY OF MODERATELY FAST REACTION IN SOLUTION

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A technique for the study of moderately fast reaction in solution up to 2000 kg/cm^2 was developed. Two types of cells were devised and applied to the thermal measurement of the cationic polymerization of tetrahydrofuran and spectrophotometric one on the reaction of tetracyanoethylene with vinyl ethyl ether.

The present report deals with the development of a modified Grieger and Eckert's method$^{1)}$ for the high pressure study of chemical kinetics of moderately fast reaction. In order to investigate the reactions in solution whose half times are less than half an hour, it is inevitable to mix two reactants and initiate the reaction after the thermal equilibration at desired pressure and temperature. Two types of reaction cells were used. A glass cell, as shown in Fig. 1 was applied to the thermal measurement on the cationic polymerization of tetrahydrofuran (THF) initiated by triethyloxonium tetrafluoroborate($Et_3O^+BF_4^-$) in dichloromethane, and a nonmagnetic stainless steel cell(Fig. 5) was used for the spectrophotometric study of the reaction of tetracyanoethylene(TCNE) with vinyl ethyl ether(VEE) in chloroform.

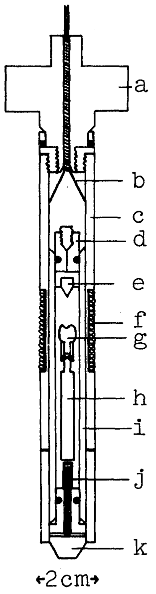


Fig. 1. Reaction cell for differential temperature measurement at high pressure.

a: high pressure plug
b: lead wire
c: cell holder
d: piston(teflon)
e: target(glass)
f: coil
g: glass ampoule
h: magnet
i: reaction cell(glass)
j: thermocouples
k: copper block

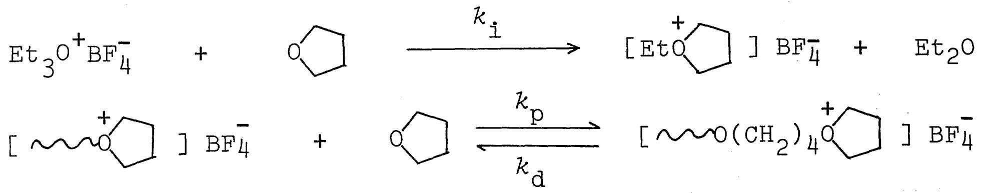
Kinetics of the Cationic Polymerization of THF by Differential Temperature Measurement

The initiator solution($Et_3O^+BF_4^-$ in CH_2Cl_2) was injected to a glass ampoule g attached at the top of the magnet h (5 mm o.d., 25 mm long) coated with teflon, and monomer solution(THF in CH_2Cl_2) was charged in the glass cell i (9.3 mm i.d., 90 mm long). A coil f was made of 0.3 mm enameled copper wire wound approximately 130 turns per cm. Five copper-constantan thermocouples j connected in a series were used to measure the differential temperature between the copper block k and a definite point in the reaction cell. After standing for a time until the thermal equilibrium was attained at the desired pressure and temperature, a few dc pulses by 6 V battery were applied to the coil until the glass ampoule broke by being hit against the target e, and the magnet was moved up and down a few times furthermore to mix well the solution.

The differential temperature caused by the extent of the reaction with reference to the copper block was recorded as a function of reaction time.

The increase of temperature due to the electric current through the coil (CH_2Cl_2 solvent) could be neglected even if about ten dc pulses were applied, while temperature rose about 0.05°C when the magnet moved in the same conditions. Moreover, temperature rise increased with the increase of the magnet diameter. The small temperature rise was suggested to be caused by the heat of stirring. It was ascertained that the temperature deviation accompanying the present technique was much smaller than that of Grieger and Eckert's method.1) They used the aluminum foil diaphragm separating two reactant solutions and found the temperature rise up to 0.5° due to electrical heating of the coil brought about by much more dc pulses required to break the diaphragm.

The cationic polymerization of THF initiated by $Et_3O^+BF_4^-$ in CH_2Cl_2 can be characterized as a living system,2-4) and proceeds simply as follows;



The temperature of the reaction system changes according to equation (1);5)

$$\frac{d\Delta T}{dt} = -k\Delta T + \alpha_p R_p \tag{1}$$

where k, R_p and α_p are the overall cooling constant, the rate of the polymerization and proportionality constant which is a function of the heat capacity of the system and the heat of the reaction. The rate of the polymerization can be given by equation (2).

$$R_p = -\frac{d[M]}{dt} = k_p[I]_0[M]_0(y_\infty - y)[1-\exp\{-k_i[M]_0\int_0^t(1-y)\}] \tag{2}$$

where $[I]_0$, $[M]_0$, y and y_∞ are the initial concentration of the initiator, the initial concentration of monomer, the conversion at the reaction time t and its equilibrium value. Integration of equation (1) gives equation (3).

$$\int_0^t\left(\frac{d\Delta T}{dt} + k\Delta T\right)dt = \alpha_p\{[M]_0 - [M]\} = \alpha_p[M]_0 y \tag{3}$$

The value of k can be experimentally determined from the cooling process of the compression heat just before initiating the reaction.5) And since one knows the conversion quenched at a known time and the value of the left hand side of equation (3) at that time, α_p can be determined. An example of the relation of $d\Delta T/dt + k\Delta T$ with reaction time is shown in Fig. 2. Combining equations (1) and (2), equation (4) is derived.

$$\ln\{\alpha_p k_p[I]_0[M]_0 - \frac{1}{y_\infty - y}(\frac{d\ T}{dt} + k\Delta T)\} = \ln\alpha_p k_p[I]_0[M]_0 - k_i[M]_0\int_0^t(1-y)dt \tag{4}$$

The value of equilibrium conversion y_∞ at 1 atm was cited from literatures3,4) and that at 1000 kg/cm^2 was calculated assuming $\Delta V = -9.5$ cm^3/mol.6)

By the graphical method as shown in Fig. 3, k_i and k_p can be determined. Some preliminary results at 40 and 1000 kg/cm^2 and 0°C are given in Table 1. The rate constants

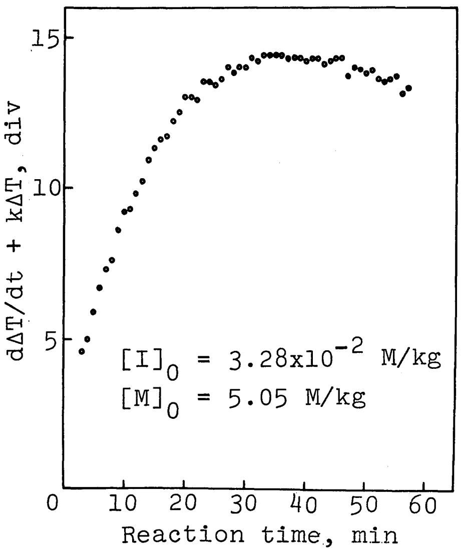


Fig. 2. Change of $(d\Delta T/dt) + k\Delta T$ with time at 0°C, 1000 kg/cm^2

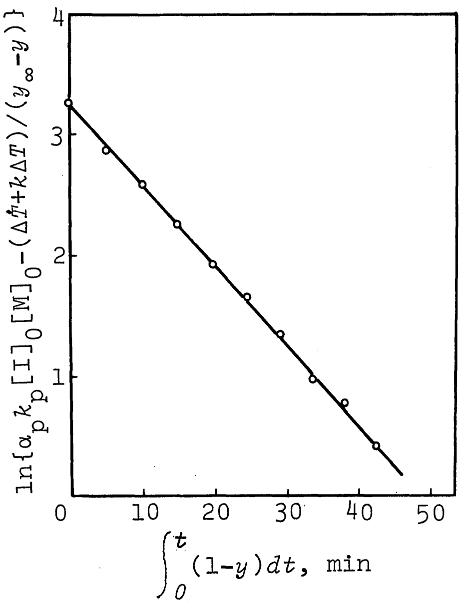


Fig. 3. Plot of equation (4)

at 40 kg/cm^2 was close to the values reported by other workers at 1 atm,[2-4] and the present method was found to be useful to study the moderately fast reaction in solution under high pressure.

Table 1. Values of k_i and k_p at 0°C

Pressure/kg cm^{-2}	40	1000
k_i/kg M^{-1} min^{-1}	8.99x10^{-3}	1.27x10^{-2}
k_p/kg M^{-1} min^{-1}	0.15	0.22

The Spectrophotometric Measurement on the Reaction of TCNE with VEE

The high pressure cell for the spectrophotometric study is shown in Figs. 4 and 5. Figure 4 is the general high pressure assemblages. The cell holder b with two guide pins for the inner cell (Fig. 5) made of nonmagnetic stainless steel was put between two sapphire windows c so as to rotate around the light axis. Another cell holder e wound with enameled wire d was put into the high pressure bomb so that the head of the holder could fit to the guide bore of the holder b. Figure 5 is the reaction cell made

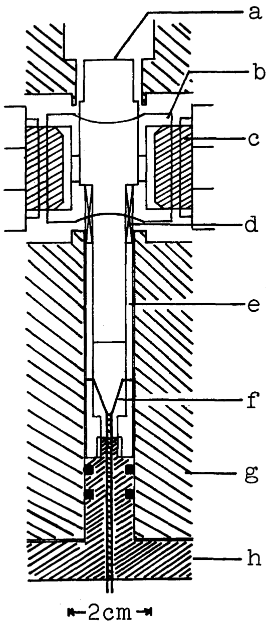


Fig. 4. High pressure cell assemblage for spectrophotometric study.

a: reaction cell
b: cell holder
c: sapphire window
d: coil
e: cell holder
f: lead wire
g: high pressure bomb
h: high pressure plug

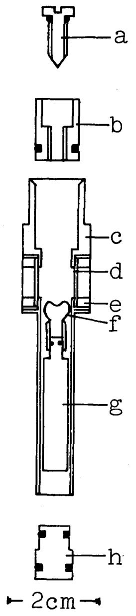


Fig. 5. Reaction cell for spectrophotometric measurement at high pressure.

a: target
b: piston
c: reaction cell
d: quartz disk
e: screw bolt
f: glass ampoule
g: magnet
h: plug

of non magnetic stainless steel with quartz disks d (the path length is 8 mm) which are sealed against the well polished planes of the cell by means of the ring-shaped screw bolts e. The grooves outside the cell body c support easily the reproducible positioning with the help of pins inside the cell holder (Fig. 4 b). The operation is almost similar to the case described in the previous section. This high pressure cell was tested up to 2000 kg/cm^2. The mixing was satisfactory within 5 sec if the foams disappeared completely by applying pressure. An utmost care should be taken to fix the inner cell, because even a slight tremor of the cell caused by moving the magnet produced a considerable error in the measurement of the light intensity.

The technique was applied to the reaction of TCNE with VEE to form an electron-donor-acceptor complex(EDA-complex) proceeding further to the cycloaddition$^{7)}$. On the other hand, the cycloaddition reaction has been understood to occur via a 1,4-dipolar intermediate(a kind of zwitterions).$^{8,9)}$ The pressure effects on similar but slower systems were reported by Kelm and coworkers$^{10)}$ who supported a zwitterionic mechanism. However, the role of the EDA-complex is still premature.

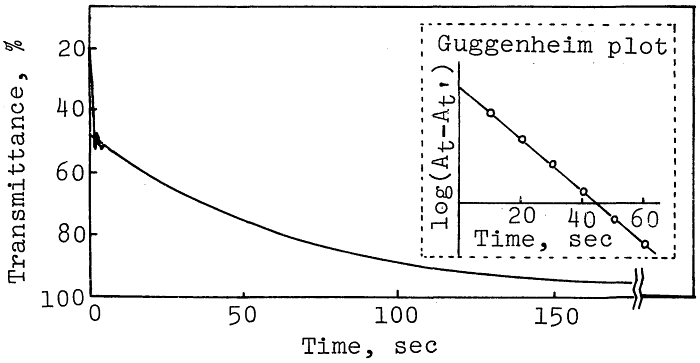


Fig. 6. Change of transmittance with time and Guggenheim plot of absorbance at 25°C, 500 kg/cm^2. $[TCNE]_0 = 3.2\times10^{-3}$M/kg, $[VEE]_0 = 0.21$ M/kg.

The change of the transmittance at 428 nm with time is shown in Fig. 6 at 500 kg/cm^2. The fluctuation at the initial stage was caused by the movement of the magnet. The Guggenheim plot is quite satisfactory, giving the value $k_{obs} = 9.1\times10^{-2}$ kg M^{-1} sec^{-1} when $[VEE]_0=0.21$ M/kg, at 25°C and 500 kg/cm^2. The expression of k_{obs} is given by either $k_{obs}=Kk_c/(1+K[VEE]_0)$ or $k_{obs}=k_c/(1+K[VEE]_0)$, where K is the equilibrium constant for the formation of EDA-complex and k_c is the rate constant for the cycloaddition, depending on the reaction scheme.$^{7b)}$ And so, k_{obs} should be further a function of $[VEE]_0$. The study of the dependency of k_{obs} on $[VEE]_0$ under pressure and pressure effect on K are going on in order to elucidate the pressure effect on each reaction step.

The authors are indebted to Mr. F. Amita for machining of the cells.

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(Received September 30, 1976)