PHOTOCHEMICAL HYDROLYSIS OF m-NITROANISOLE

UNDER HIGH PRESSURE

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The photochemical hydrolysis of m-nitroanisole was studied at room temperature under high pressure up to 3000 kg/cm².* The quantum yield to produce m-nitrophenolate ion in alkaline medium decreased with pressure. That behavior was explained by the difference of the pressure effects on the elimination step of hydroxide ion and that of methoxide ion from the excited σ-complex, the existence of which was already postulated by Havinga and his co-workers.

Introduction

To the behavior of excited molecules in a condensed phase under high pressure has been recently paid much attention in views of the fluorescence quantum yields[1-3] and excimer or exciplex formation equilibria[4-8]. The dissociation equilibria of some aromatic alcohols were also studied by the fluorescence measurement[9]. The "*in situ*" kinetics of chemical reactions in solution induced by the photo-irradiation under high pressure was little performed. Perhaps because the lack of the knowledge of the pressure effects on the inherent photochemical and photophysical processes may have made the interpretation of the experimental results uncertain. The cage effect of pair radicals photochemically produced from azobisisobutyronitrile in the presence of DPPH[10] and the photo-dimerization of anthracene[11] were studied by Osugi and co-laborators. In the present paper, the authors deal with the pressure effect on the quantum yield of the photochemical hydrolysis of m-nitroanisole in aqueous alkaline solution at room temperature. This reaction system is known to produce a single photochemical product[12].

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Experimentals

Materials

m-Nitroanisole (Nakarai Chemicals Ltd.) was three times recrystallized from methanol-water mixture (mp, 39°). The aqueous alkaline solutions of the desired concentrations were prepared by dilution from the commercially obtained standard solution of sodium hydroxide with distilled water. and the exact concentration was redetermined by titration. Potassium ferrioxalate was prepared and used as an actinometer in the fasion developed by Hatchard and Parker[13].

Apparatus

The schematic layout of the high pressure apparatus is shown in Fig. 1, and the high pressure vessel in Fig. 2, which are essentially the same as those previously used[3, 11] but with a few modifications so that the pressure can be applied to the sample solution through a piston b from a pressure generating pump without using an intensifier. The pressure was determined by a manganin coil calibrated for a Heise Bourdon gauge. The pressure range in this study is up to 3000kg/cm². The high pressure vessel has two sapphire windows in horizontal direction and one in vertical direction. Silicone oil (Toshiba: TSF 451, 200cps) which was completely transparent at the wavelengths longer than 300nm. was used as the pressure transmitting fluid, and made fresh for each experimental run. The inner cell c made of stainless steel has three quartz windows, two for the monitoring and one for the irradiation. The optical path for the monitoring is of 0.79 cm. The inner cell was supported by three sapphire windows so as to be fixed reproducibly. Since the measurement at the atmospheric pressure. using this inner cell, was not reproducible because of the difficulty of removal of the foams, the data at 50 kg/cm² was taken as equal to those at 1 atm.
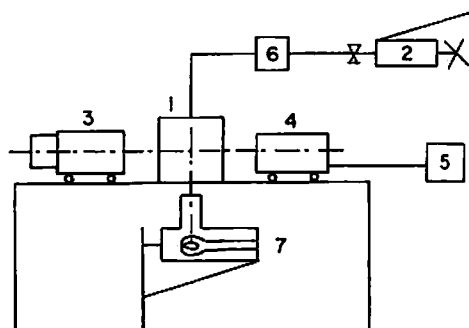

Fig. 1 Schematic layout of high pressure apparatus. 1: high pressure vessel, 2: pump, 3: tungsten lamp and monochromator. 4: photomultiplier, 5. recorder, 6: manganin gauge, 7: high pressure mercury lamp

Procedure

The alkaline solution of *m*-nitroanisole (*m*-NA). the solvent being methanol/water mixture (MeOH/H$_2$O=4/96. 2/98 v/v), injected in the high pressure cell was irradiated through an interference filter (λ_{max}=366nm, $\Delta\lambda_{1/2}$=48nm) using a high pressure mercury lamp (USHIO UM-102, 100W). The change of the absorbance of the product was monitored by a single-beam spectrophotometer (Hitachi-139) at 425nm where the absorption of *m*-nitrophenolate ion existed but with

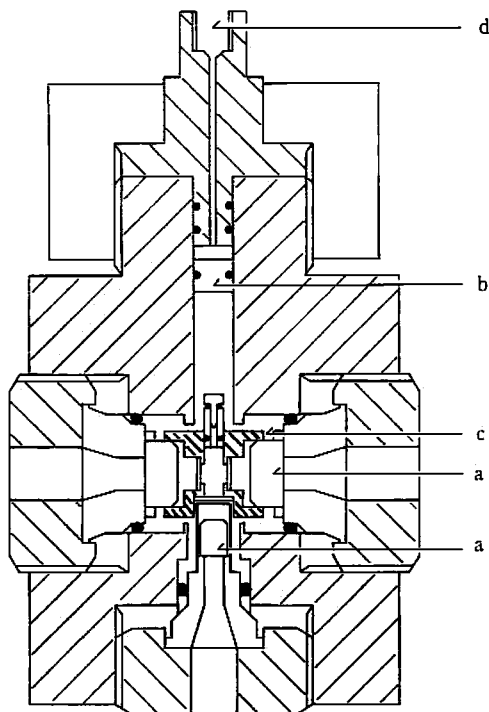13) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, A235, 518 (1956)

Fig. 2 High pressure Vessel.
a : sapphire window, b : piston, c : inner cell (stainless steel with three quartz windows), d : oil inlet

no absorption due to *m*-NA. Since the measurements were often necessary to be carried out for a long period, the intensity of the transmitted light was checked at intervals at 560nm where the reaction solution was transparent during the reaction. The irradiation was carried out both in the presence and absence of the dissolved air. The solution was degassed, if necessary, by the freeze-pump-thaw method and charged into the cell in the nitrogen atmosphere.

Results

The spectral change with the irradiation at 1 atm is shown in **Fig. 3**, where three isosbestic points exist. The final spectrum exactly coincides with that of *m*-nitrophenolate ion which can be prepared separately by addition of *m*-nitrophenol to an alkaline solution. So the photochemical product is found to be only *m*-nitrophenol, dissociating into *m*-nitrophenolate ion, *m*-NP⁻, in the alkaline medium. The high pressure experiments were done under the condition that *m*-nitrophenol almost completely converted to the phenolate ion.

The increases of *m*-NP⁻ with the irradiation at some hydroxide ion concentrations are shown in Figs. 4, 5 and 6. The pressure obviously makes the retarding effects on this photochemical reaction. At each pressure the increase of hydroxide ion concentration enhances the rate of the photo-hydrolysis. The quantum yields were determined by the way mentioned below.
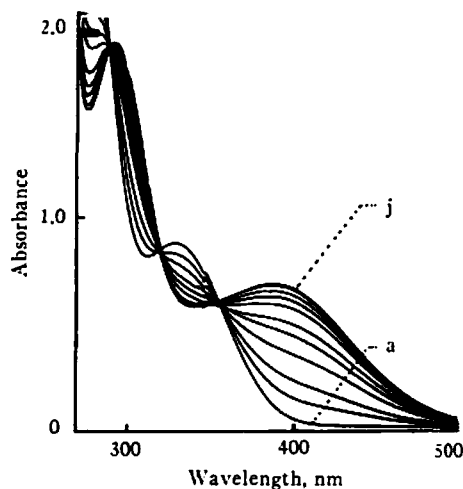
A basic relation is given by Eq. (1).

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Fig. 3   Chage of the absorption spectra by the irradiation at 1 atm. $[OH^-]/[m\text{-}NA]_0 = 45.1$, $[m\text{-}NA]_0 = 2.21 \times 10^{-4} mol/l$, MeOH : 2 vol%, irradiation time (min): a) 0 to j) 25
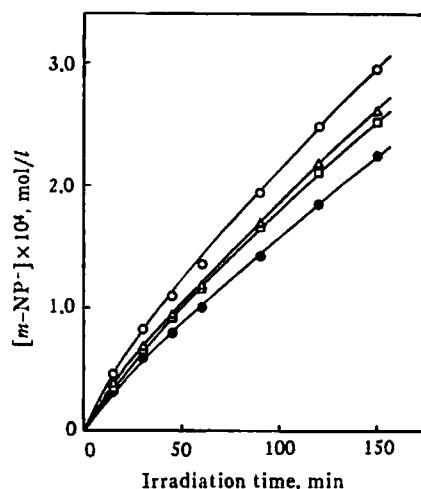
Fig. 4   The increase of $m\text{-}NP^-$ with irradiation time (irradiated at 366 nm). $[OH^-]/[m\text{-}NA]_0 = 95.1$, $[m\text{-}NA]_0 = 8.15 \times 10^{-4}$ mol/l, MeOH : 4 vol%. Pressure (in kg/cm²) is ○: 50, △: 1000, □: 2000, and ●: 3000.

Fig. 5   The increase of $m\text{-}NP^-$ with irradiation time. The experimental conditions and symbols are same as those of Fig. 4, except $[OH^-]/[m\text{-}NA]_0 = 24.0$.
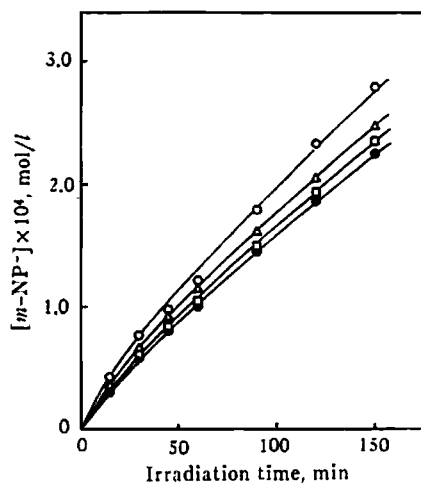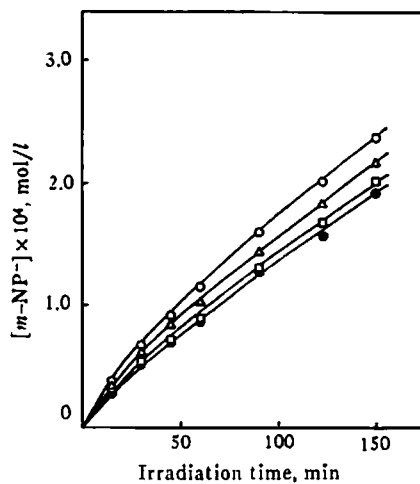
Fig. 6   The increase of $m\text{-}NP^-$ with irradiation time. The experimental conditions and symbols are same as those of Fig. 4, except $[OH^-]/[m\text{-}NA]_0 = 9.47$.

$$\frac{dC}{dt} = I_{abs} \cdot \Phi, \tag{1}$$

where C represents the photo-product concentration, I_{abs} the number of absorbed photons, and Φ the quantum yield. The facts that the absorption of the irradiating light is not complete in the present system, and that the light is partly shielded by m-NP$^-$ accumulated during the irradiation, should be taken into account. Then, Eqs. (2), (3) and (4) are derived,

$$\frac{dC}{dt} = \Phi I_0 \exp(-\varepsilon_p C_p l)[1 - \exp\{-\varepsilon(C_0 - C_p)l\}], \tag{2}$$

$$= \Phi I_0 A, \tag{3}$$

$$A = \exp(-\varepsilon_p C_p l)[1 - \exp\{-\varepsilon(C_0 - C_p)l\}], \tag{4}$$

where ε and ε_p are the absorption coefficients of the reactant and product at the irradiating wavelength, C_p the photo-product concentration which can be calculated from the absorbance and absorption coefficient at 425nm, C_0 the initial concentration of m-NA, and l the optical path length of the irradiating light. I_0 is the number of photons per liter, being specific to the set of the used apparatus and determined by use of a potassium ferrioxalate actinometer. The factor $\exp(-\varepsilon_p C_p l)$ corresponds to the inner filteration due to the product, and $[1 - \exp\{-\varepsilon(C_0 - C_p)l\}]$ to the factor absorbed by the reactant m-NA. Figs. 7 and 8 show the plots of Eq. (3), in which, though the experimental points are a little scattered, the least square calculation for the assumed straight line passing the origin gives the value of ΦI_0. In Table 1 are given the quantum yields. At 50 kg/cm², the value of Φ, 0.27 at high hydroxide concentration is comparable to 0.225 at 313nm as reported by de Jough et al.[12] The quantum yield slightly but distinctly decreased with the pressure.
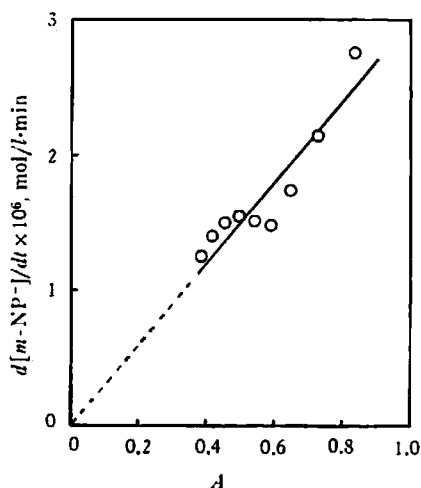

Fig. 7 Relation between $d[m\text{-NP}^-]/dt$ and A in Eq. (3) at 50 kg/cm². The data points were calculated from the curve of Fig. 6.
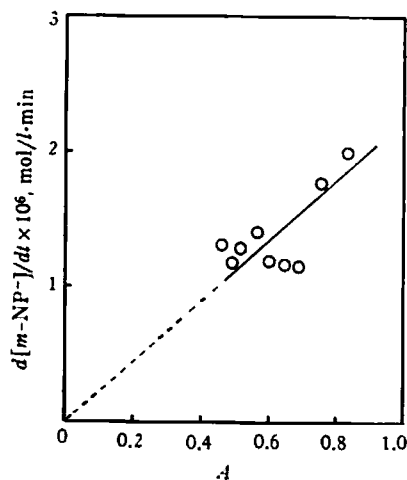
Fig. 8 Relation between $d[m\text{-NP}^-]/dt$ and A in Eq. (3) at 3000 kg/cm². The data points were calculated from the curve of Fig. 6.

Table 1   Quantum yield, Φ, of the photochemical hydrolysis of m-NA in the presence of dissolved air. $[m\text{-NA}]_0 = 8.15 \times 10^{-4}$ mol/l, MeOH : 4 vol %

[OH$^-$]† . mol/l \ P. kg/cm^2	50	1000	2000	3000
7.72×10^{-3}	0.21	0.18	0.16	0.15
19.6×10^{-3}	0.24	0.20	0.19	0.15
77.5×10^{-3}	0.27	0.22	0.21	0.18

†concentration determined at atmospheric pressure

Considerations

The nucleophilic substitution of ground-state benzenoid molecules is well known to be facilitated for the *meta*-position of an electron-releasing substituent and for the *para* of an electron-withdrawing one. In the marked contrast to these facts, the excited-state molecule of m-nitroanisole easily solvolyzes. This difference of the reactivity between the ground-state and excited-state has been successfully interpreted by the simple MO calculation[14]. The electron withdrawal of the *meta*-position of a nitro-substituted excited molecule makes the nucleophilic attack favorable. The excited state undergoing the efficient photochemical substitution was reported to be a triplet state[15], but the authors could not find any distinct effect of the dissolved air on the quantum yield of the photochemical hydrolysis, which is in accordance with the result by de Jongh *et al*.[12]

de Jongh *et al*. postulated the following photochemical reaction scheme[12].
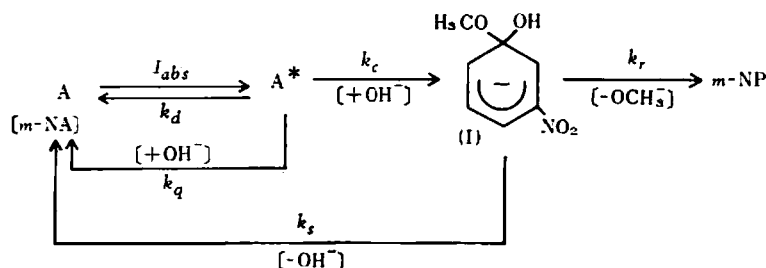
The formation of an excited σ-complex (I) as an intermediate was inferred from the ^{18}O-labeling experiment[12] in which the fission of the ring carbon-^{18}OCH$_3$ bond took place. The above scheme being taken into account, the relation between $1/\Phi$ and $1/[\text{OH}^-]$ can be derived, Eq. (5).

$$\frac{1}{\Phi} = \frac{k_d(k_r + k_s)}{k_c \cdot k_r} \cdot \frac{1}{[\text{OH}^-]} + \frac{(k_c + k_q)(k_r + k_s)}{k_c \cdot k_r} \tag{5}$$

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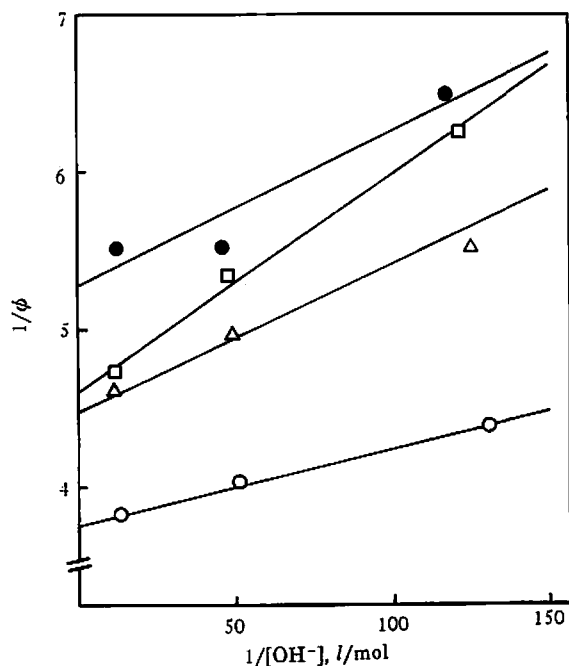
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Fig. 9 Dependence of quantum yields on hydroxide ion concentration. $[m\text{-NA}]_0 = 8.15 \times 10^{-4}$ mol/l, MeOH : 4 vol%. The symbols are same as those of Fig. 4.

Table 2 The coefficients of $1/\Phi$ vs $1/[OH^-]$ plot.
$[m\text{-NA}]_0 = 8.15 \times 10^{-4}$ mol/l, MeOH ; 4 vol %, 19°C

P (kg/cm²)	Slope, $\dfrac{k_d(k_r+k_s)}{k_c k_r}$	Intercept, $\dfrac{(k_c+k_q)(k_r+k_s)}{k_c k_r}$
50	9×10^{-3}	3.7
1000	9×10^{-3}	4.5
2000	14×10^{-3}	4.6
3000	10×10^{-3}	5.3

The plots of $1/\Phi$ vs $1/[OH^-]$ are shown in Fig. 9. The values of the slopes and the intercepts are listed in Table 2. As seen, the pressure increases the value of the intercept, that is, the following relation is given,

$$\left(1+\frac{k_{q(p)}}{k_{c(p)}}\right)\left(1+\frac{k_{s(p)}}{k_{r(p)}}\right) > \left(1+\frac{k_{q(1)}}{k_{c(1)}}\right)\left(1+\frac{k_{s(1)}}{k_{r(1)}}\right), \tag{6}$$

where subscripts (p) and (1) represent high pressure and atmospheric pressure, respectively. In addition reaction of an ion, k_r is considered to be increased by pressure as generally found in the ground-state SN_2 reactions[16], in which the volumes of activation are around -9 cm³/mole. The volume decrease connected with the excimer or exciplex formation was found to be $16\text{–}22$ cm³/mole[5,6].

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16) S. D. Hamann, "Physico-Chemical Effects of Pressure", Chapter 9, Butterworth Sci. Pub., London (1957)

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Even if this process is of diffusion-controlled reaction, since the mobility of the hydroxide ion is known to increase with pressure up to 3 kbar[17], k_c will increase with pressure. In any event, $k_{c(p)} > k_{c(1)}$. The quenching process k_q is a diffusion-controlled simple bimolecular collision, and so the decrease of the reaction rate with pressure, corresponding to the increase of viscosity is reasonably expected[9]. Then the relation, Eq. (7), is obtained.

$$\frac{k_{q(p)}}{k_{q(1)}} < \frac{k_{c(p)}}{k_{c(1)}} \tag{7}$$

Moreover, considering that the elimination processes of methoxide and hydroxide ions accompany the bond expansion without changing the overall electronic charge, both k_r and k_s should be retarded by pressure. Then, from Eqs. (6) and (7), Eq. (8) can be derived.

$$1 > \frac{k_{s(p)}}{k_{s(1)}} > \frac{k_{r(p)}}{k_{r(1)}} \tag{8}$$

This relation can be interpreted by the relative strength of the electrostriction caused by hydroxide and methoxide ions. Since the smaller ion, hydroxide ion, may cause the stronger electrostriction than methoxide ion, the retardation of k_s by pressure will be less than that of k_r.

The variation of the slope of Fig. 9 with pressure does not indicate any tendency perhaps because of low accuracy of the determination. However, it will be worthwhile to see what factors are concerned. The pressure dependence of k_d is unknown, but it will be reasonably pressumed that the radiationless energy transfer to the surroundings may be, at least, promoted in the denser medium, though the degree of the enhancement will be small. As mentioned above, both k_c and k_s/k_r are also expected to be enhanced by pressure, so that the variation of the term, $k_d(1 + k_s/k_r)/k_c$, will be controlled by the balance of these factors.

In conclusion, the decrease of the quantum yield of the photochemical hydrolysis of m-nitroanisole with increasing pressure is mainly ascribable to the more retardation of methoxide ion elimination (k_r) than hydroxide ion elimination (k_s), which is explained by the general electrostriction concept of ionic solution.

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