[November, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 3061—3067 (1985) 3061

Kinetic Study of the Decay of Chlorine Dioxide in Supercooled and Glassy Organic Solvents

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(Received January 18, 1985)

Chlorine dioxide (ClO_2), which is a stable free radical, decayed in supercooled and glassy liquid 3-methylhexane (3MHX) and 3-methylpentane near their glass transition temperatures (T_g's). The decay of ClO_2, however, was not observed in toluene or 2-methyl-1-propanol. The kinetic analysis of the decay of ClO_2 in 3MHX is reasonably explained by its diffusional motion and dimer formation. The diffusion constants of ClO_2 in 3MHX at temperatures around T_g were estimated in the analysis.

Chlorine dioxide (ClO_2) is well-known to be a stable free redical at room temperature. It was found, however, that ClO_2 decayed in glassy and supercooled liquid 3-methylhexane near its glass transition temperature (T_g) and reappeared at temperatures higher than T_g by about 40 K. These observations have not previously been reported, hence there is a need to explain the mechanism responsible for this decay. The behavior of ClO_2 in some other organic glassy and supercooled liquids is also described.

Experimental

Chlorine dioxide was synthesized by dropping sulfuric acid into a mixture of potassium chlorate and oxalic acid, followed by a passage through an aqueous solution of sodium hydroxide and drying on phosphorus pentaoxide (P_2O_5). The product was further dried over P_2O_5 under vacuum and stored in a glass reservoir in a freezer to prevent decomposition.

3-Methylhexane and 3-methylpentane (99% purity) were purchased from Aldrich Chemicals Co. and heptane, toluene, and 2-methyl-1-propanol (ISB) were reagents of guaranteed grade from Wako Pure Chemicals. These materials were further purified by the methods recommended in the literature.[1] Purity of ISB was 99.54% and the impurities in the other materials were less than 0.01% on gas chromatographic analysis. The purified materials were dried under vacuum and stored in glass ampules. To avoid contamination from vacuum grease in storage, greaseless stopcock with Teflon plunges and ball joints with Teflon O-rings were used.

The purified solvent was degassed by several freeze-pump-thaw cycles and distilled into a calibrated measuring tube under vacuum. A desired amount of solvent was then distilled from the tube into a quartz tube for ESR measurement. Gaseous ClO_2 was taken from the reservoir to an ampule of known volume and introduced into the quartz tube by condensation. The amount of ClO_2 added to the solvent was determined from the volume of the ampule and the pressure of ClO_2. The vapor pressure of ClO_2 was estimated from the temperature of the reservoir. The sample solutions sealed in the ESR tubes were stored in a freezer to prevent loss of ClO_2.

ESR measurements were carried out using a home-built X-band spectrometer equipped with a cryostat using a stream of nitrogen as refrigerant. The cryostat was able to maintain a sample at any temperature from 79 K to 200 K within ±0.1 K for any desired period. The ESR spectrometer consisted of a homodyne-detection system with 450 kHz field modulation. The change in the sensitivity of the ESR measurement was monitored with manganese oxide doped in magnesium oxide.

Usually, the sample solution was kept at 200 K for 3 h to establish the saturation of ClO_2 into solvent, then vitrified by plunging in liquid nitrogen.[2] The glassy solution containing ClO_2 was immediately inserted in the sample became the same as that of the cryostat within 3 min after insertion of the sample.

Analysis of the decay of ClO_2 was carried out with a NEAC 2200/700-computer at Osaka University and a HITAC 8700-computer at Hiroshima University.

Results and Discussion

ESR of ClO_2 in glassy 3-methylhexane (3MHX) gave a pronounced anisotropic spectrum as shown in Fig. 1. When the sample solution was inserted in the cryostat at 97.0 K, the amplitude of the spectrum decreased with time as shown in Fig. 2. As the amplitude decreased, no change in the line shape was observed in the range of ±75 mT from the peak (2). Figure 3 shows the spectra for solutions at higher concentration than that of the solution whose spectrum is shown in Fig. 2 and at a different temperature. Although the difference of the ClO_2 concentration did not produce any remarkable spectral changes, the decay of the signal in the solution of higher concentration became more rapidly at 97.0 K. As the temperature of the solution was raised to 106.3 K, the ClO_2 signal was hardly observed as shown in Fig. 3(B). After the signal disappeared no precipitate was found in the solution. No ESR absorption due to a triplet-state molecule in the g=4 region was descernible even at a gain 200 times greater. On further heating a nearly isotropic

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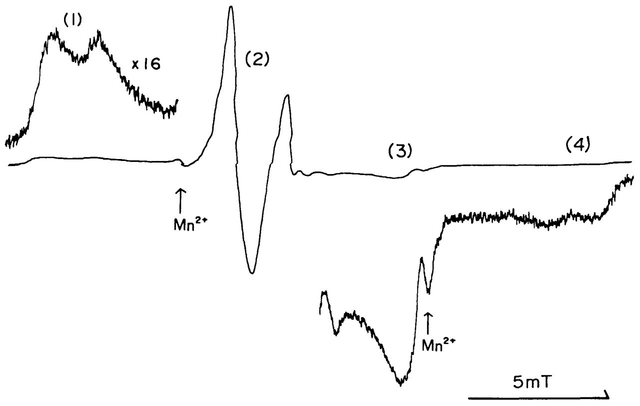

Fig. 1. The ESR spectrum of ClO_2 in 3MHX at 77 K. Peaks indicated by arrows are signals from Mn^{2+} in MgO for the field-calibration.

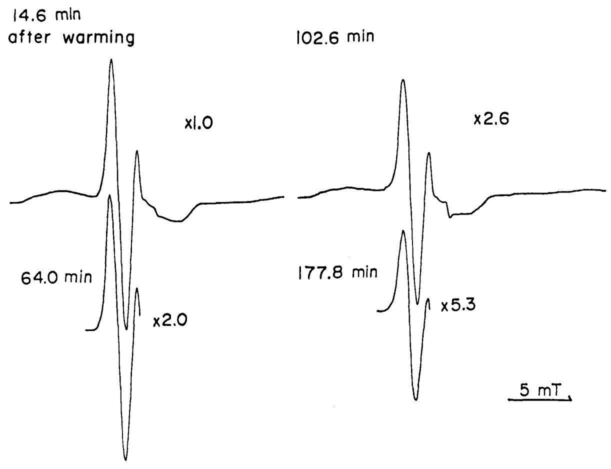

Fig. 2. The ESR spectra of ClO_2 in 3MHX containing ClO_2 of 4.5×10^{-3} mol dm^{-3} at 97.0 K.

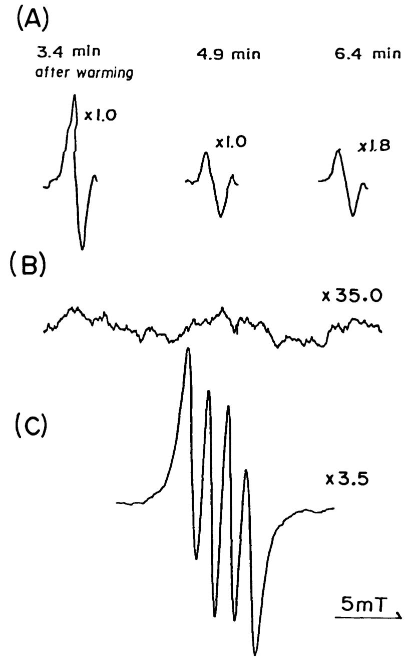

Fig. 3. The ESR spectra of ClO_2 in 3MHX containing ClO_2 of 1.8×10^{-2} mol dm^{-3} at various temperatures: 97.0 K (A), 106.3 K (B), and 131.6 K (C).

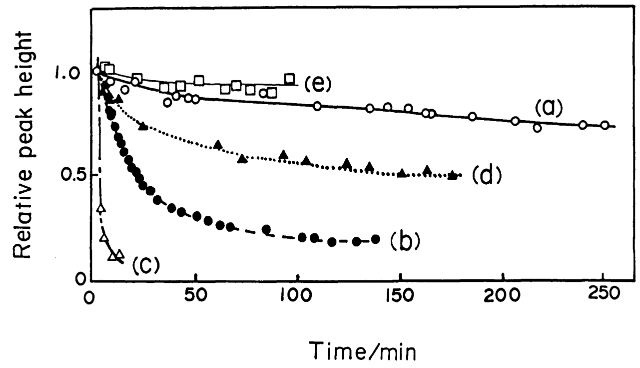

Fig. 4. The decay of peak (2) of Fig. 1 in 3MHX containing ClO_2 of 1.1×10^{-2} mol dm^{-3} at various temperatures: at 87.9 K (a), 96.2 K (b), 105.8 K (c), 115.7 K (d), and 125.3 K (e). The peak heights are normalized by the peak height of the first measurement.

spectrum of Fig. 3(C) for ClO_2 appeared at 131.6 K. As the solution was heated after vitrification and subsequent reinsertion in the cryostat at 97.0 K, the same results were obtained.

ClO_2 in 3-methylpentane (3MP) decayed near 80 K. The decay of ClO_2, however, was not observed in the supercooled and glassy liquids of toluene and 2-methyl-1-propanol (ISB) or in polycrystalline heptane at temperatures ranging from 79 K to about 200 K.

The decay of ClO_2 could be caused by the reaction of ClO_2 with impurities of the solvents and/or oxygen. On consideration of the high purities of the solvents and the use of degassed solutions, those reactions are not responsible for the decay. Besides ClO_2, chlorine monoxide and chlorine trioxide are paramagnetic. As their ESR spectra[3] differ from the spectra of ClO_2, the change of ClO_2 to the monoxide or the trioxide is not able to explain the results. No other phase transitions of 3MHX and of 3MP near their glass transition temperatures (88 K[4] and 77 K[5]), besides the glass transitions, have been reported as far as we know.

Figure 4 shows the decay of peak (2) in 3MHX at various temperatures near T_g. At 77 K, where 3MHX is in the glassy state, ClO_2 gradually decayed with a half life of one week. When the temperature was raised, the rate of decay increased between 77 K and 105 K, however, it decreased above 105 K.

Figure 5 shows the decay of ClO_2 at various

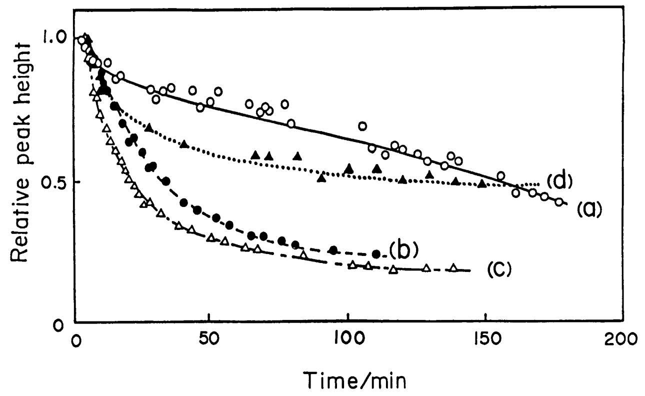

Fig. 5. Additive effect of ClO_2 on the decay of peak (2) of Fig. 1 in 3MHX at 96 K. The nominal concentration of ClO_2 are: 1.6×10^{-3} mol dm^{-3} (a), 5.5×10^{-3} (b), 1.1×10^{-2} (c), and 3.5×10^{-2} (d). The peak heights are normalized by the peak height of the first measurement.

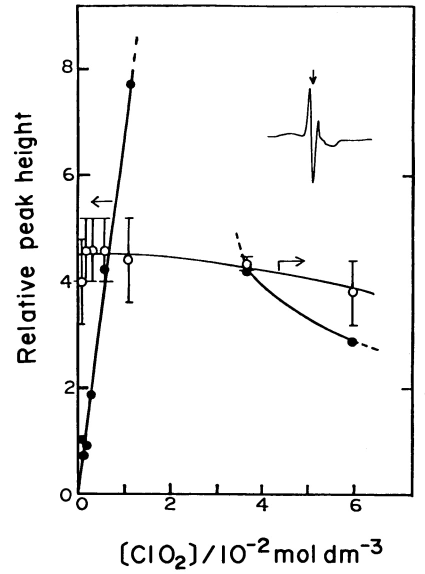

Fig. 6. Additive effect of ClO_2 on the heights and widths of peak (2) of Fig. 1 in 3MHX at 77 K.

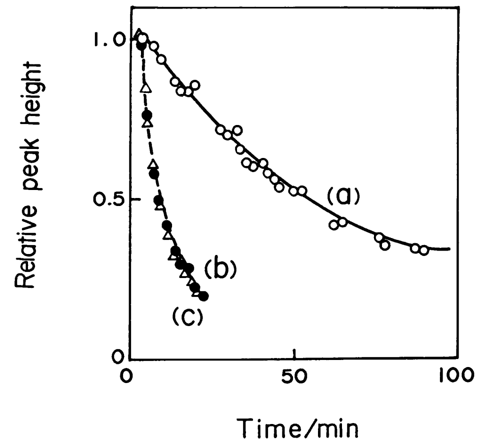

Fig. 7. The decay of peak (2) of Fig. 1 in 3MHX containing ClO_2 of 4.3×10^{-2} mol dm^{-3} at 105.9 K on various thermal treatments of the samples. Lines (a), ○; and (b), ●, are obtained after immediate inserition of the samples from 200 K and 77 K, respectively, into the cryostat of 105.9 K. After annealing for 1 d at 77 K, line (c), △, was obtained. The peak heights are normalized by the peak height of the first measurement.

nominal concentrations at 96.0 K. The concentrations were calculated from the added amounts of ClO_2 and the volume of the solvent at 77 K which was estimated from its density at 77 K.[6] The decay is faster with addition of ClO_2 until the concentration was increased at about 2×10^{-2} mol dm^{-3}. When the concentration is at 3.5×10^{-2} mol dm^{-3}, the decay slows down.

The plots of the widths and the heights of the peak (2) are shown in Fig. 6 against the nominal concentration of ClO_2 at 77 K. The peak widths seem to be effectively independent of the concentration. Assuming no change of ESR lineshape with the ClO_2 decay, the independence of the peak widths on the nominal concentration indicates that change of ClO_2 concentration can be related to the ESR peak-heights. The heights linearly increase with the addition of ClO_2 up to 1×10^{-2} mol dm^{-3}. In the range of the concentration, $(4-6)\times10^{-2}$ mol dm^{-3}, the peak heights gradually decrease with the addition of ClO_2. In this range the precipitation of ClO_2 was not observed. The decrease of the peak heights at high ClO_2 concentration will be discussed later.

Analysis of the Decay of ClO_2. Taking into consideration the above results, we assumed that the decay of ClO_2 in 3MHX is due to the formation of a diamagnetic dimer of ClO_2 ($[ClO_2]_2$) described in Eq. 1.

$$ClO_2 + ClO_2 \rightarrow [ClO_2]_2. \qquad (1)$$

The dissociation of the dimer was considered in the explanation of the temperature dependence of the decay shown in Fig. 4. The diffusional motion of the ClO_2 molecule was also taken into consideration of the decay because of the high viscosity of 3MHX (about 10^{17} Pa s at T_g[7]).

Before analyses of the curves in Figs. 4 and 5 it is necessary to decide whether the initial distribution of ClO_2 is uniform or not.[8] Figure 7 shows the effects of various thermal treatments of the samples on the decay of the peak (2) of Fig. 1. The curves (a) and (b) were obtained after immediate insertion of the samples into the cryostat of 105 K from 200 K and 77 K, respectively. When the sample was inserted into the cryostat of 105 K after annealing for 1 d at 77 K, the curve (c) was obtained. No uniform distribution of the ClO_2 molecules resulting from rapid cooling presumably accelerates the decay.

Waite obtained solutions of the kinetic equations of the diffusion-controlled bimolecular reaction $A+B \rightarrow AB$ with some boundary condition.[9] His theory has been applied and also extended to the analyses of the annealing of the radiation defects in the solid by several authors.[10] We applied Waite theory to the analysis of the decay of ClO_2 considering the reversibility of the reaction (Eq. 1).

According to his theory, the change in the ClO_2 concentration will be expressed by the change in the joint probability density $\rho_{ij}(t)$ between the *i*th reactant and the *j*th reactant at time *t*. As Waite demonstrated, the $\rho_{ij}(t)$ satisfies

$$D_i\nabla_i^2\rho_{ij}(t) + D_j\nabla_j^2\rho_{ij}(t) + f_{ij}(t)\rho_{ij}(t) = \partial_{ij}\rho(t)/\partial t, \tag{2}$$

where $f_{ij}(t)$ act as time-dependent chemical rate-of-raction coefficients. D_i and D_j are the diffusion constants of the *i*th and *j*th reactants, respectively; for the ClO_2 decay, $D_i=D_j=D$. The boundary conditions are given as

$$\rho_{ij}(t) = \rho_{\mathrm{eq}} \qquad \text{for } r \leqq R_0, \tag{3}$$

and

$$\rho_{ij}(t=0) - \rho_{\mathrm{eq}} = N\exp[-r^2(\lambda R_0)^{-2}] \qquad \text{for } r>R_0. \tag{4}$$

ρ_{eq} is the equilibrium joint probability, $r=|r_i-r_j|$, and R_0 is the radius of the capture sphere. N is a normalization constant and λ is a parameter to be determined from the experimental data. The boundary conditions show that at $r=R_0$ ClO_2 molecules over the equilibrium concentration (which may be propotional to solubility of ClO_2 in 3MHX) immediately react with the other molecules and the initial distribution of ClO_2 molecules is expressed by Eq. 4. Using the boundary conditions, we solved Eq. 2 and rewrote the solution in terms of the fraction of the decay ψ. The results are:

$$\begin{aligned} \mathrm{d}\psi/\mathrm{d}t = {} & 2\pi R_0^3C_0'(\psi_{\mathrm{eq}}-\psi)^2z(1+2\pi^{-1/2}z^{-1}) \\ & + 2\pi R_0^3[2\pi^{-1/2}\exp(-\lambda^{-2})\lambda^4(z^2+\lambda^2)^{-2} \\ & + \{2\lambda^2(z^2+\lambda^2)^{-1}-4\lambda^2(z_z+\lambda^2)^{-2}\} \\ & \times \lambda z(z^2+\lambda^2)^{-1/2}\exp\{-(z^2+\lambda^2)^{-1}\} \\ & \times \mathrm{erf}\{\lambda^{-1}z(z^2+\lambda^2)^{-1/2}\}](1-\psi_0)N \\ & \times \exp(\int_0^t f_{ii'}\mathrm{d}t), \end{aligned} \tag{5}$$

where

$$\int_0^t f_{ii'}\mathrm{d}t = -\int_0^z 4\pi R_0^3C_0'(\psi_{\mathrm{eq}}-\psi)(z+2\pi^{-1/2})\mathrm{d}z, \tag{6}$$

$$\mathrm{erf}(x) = \int_x^{\infty}\pi^{-1/2}\exp(-\alpha^2)\mathrm{d}\alpha, \tag{7}$$

$$\psi = (C_0'-C)/C_0', \tag{8}$$

and

$$z = (8Dt/R_0)^{1/2}. \tag{9}$$

C is the concentration of ClO_2 at time t and C_0' is the concentration of the first measurement. ψ_{eq} is the equilibrium fraction of the decay. For short times such that $8Dt \ll (\lambda R_0)^2$,

$$\psi - \psi_0 \simeq 8^{1/2}R_0^3N\exp(-\lambda^{-2})(2Dt)^{1/2}, \tag{10}$$

where ψ_0 is the fraction of the decay at time $t=0$. Equation 10 indicates that at short times ψ is propotional to the square root of t. The Runge-Kutta technique was used in the computer-assisted evaluation of Eq. 5. The parameters taken in this calculation were ψ_0, ψ_{eq}, λ, R_0, and the initial slope of the plots of ψ *versus* $t^{1/2}$.

The best fits of ψ for the temperature dependence of the decay below 105 K (in Fig. 4) are shown in Fig. 8 as a function of $t^{1/2}$ with the experimental points of ψ. The results that at early stages ψ is propotional to $t^{1/2}$ agree with the expectations from Eq. 10. Table 1 summarizes some parameters used in those calculations. Decrease of R_0 with temperature is considered to indicate greater solvation of ClO_2. At a distance of λR_0 the probability density of other molecules around

TABLE 1. PARAMETERS USED FOR THE SIMULATION OF THE DECAY OF ClO_2 IN 3-METHYLHEXANE AT VARIOUS TEMPERATURES[a)]

Parameter[b)]	T/K			
	77.4	87.9	96.2	105.8
λ	1	2	2.5	4
$R_0/10^{-8}$ cm[c)]	20	10	8	5
$\lambda R_0/10^{-8}$ cm	20	20	20	20
$D/10^{-13}$ cm^2 min^{-1}	5.9×10^{-6}	2.3×10^{-4}	6.0×10^{-2}	2.3

a) The nominal concentration of ClO_2 is 1.1×10^{-2} mol dm^{-3}. b) For definition see the text. c) 1 cm $=10^{-2}$ m.

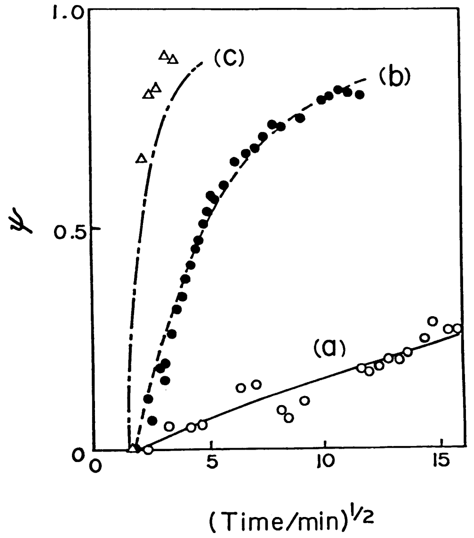

Fig. 8. The decay of ClO_2 in 3MHX containing ClO_2 of 1.1×10^{-2} mol dm^{-3} at various temperatures: 87.9 K (a), 96.2 K (b), and 105.8 K (c). The lines show the calculation by use of Eq. 5 in the text. The parameters used in these calculations are shown in Table 1.

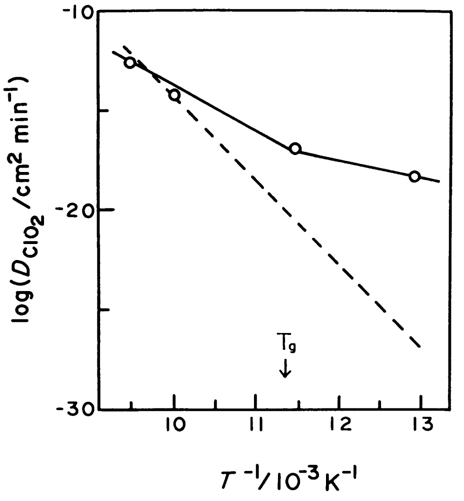

Fig. 9. The Arrhenius plots of diffusion constants of ClO_2 in 3MHX containing ClO_2 of 1.1×10^{-2} mol dm^{-3}. The open circles show the values of the constants shown in Table 1. The dashed line shows the calculation by use of Eq. 11.

one molecule has the maximum value. The constant value of λR_0 is to be expected since the sample solutions were always vitrified by plunging them into liquid nitrogen. Slower cooling of the solutions presumably produces sparse distribution of ClO_2 molecules, that is a large λR_0 value, and may retard the ClO_2 decay as shown in Fig. 7. The values of ψ_{eq} of the lines in Fig. 8 were greater than 0.98, but at $\psi_{eq}>0.975$ the calculated lines dis not change with the value of ψ_{eq}. From the estimated ψ_{eq}'s at various temperatures the change in the enthalpy of the formation of the ClO_2 dimer was estimated to be -17 KJ mol^{-1} at the lower limit. The reasonable fits of ψ for the temperature dependence over 105 K, however, were difficult to explain. As the solutions were heated to the proper temperature over 105 K, the ClO_2 molecules decayed at around 105 K. This situation probably made reasonable fits difficult.

Figure 9 shows Arrhenius plots of the diffusion constants (D's) of ClO_2. The dashed line is the plots of the diffusion constants (D_η's) calculated with Stokes-Einstein's relation given by

$$D_\eta = kT/6\pi\eta a. \tag{11}$$

Here k is the Boltzmann constant, T is the temperature, η is the viscosity, and a is the radius of the molecule. The values of η were taken from the reported values of Ling and Willard.[7] At temperatures around T_g the values of η were estimated by the extrapolation of the reported values. Below T_g the values of D are greater than those of D_η. Above T_g the values of D seem to be near those of D_η. The value of Arrhenius E factor of η was reported as 79 KJ mol^{-1},[7] while the value of D was estimated to be 68 KJ mol^{-1} above T_g.

The plots show that at T_g a translational motion of ClO_2 is accelerated. On the other hand the rotational correlation time of ClO_2 in 3MHX did not show any clear changes at T_g.[11] Seki *et al.*[12] studied the polymerization of vinyl acetate in the glassy state by differential thermal analyses and showed that it polymerizes at temperatures just above T_g, *i.e.* in the supercooled state. They considered that certain immobilized "motion freedom" in the glassy state melts at just above T_g and makes possible the rearrangement and the diffusion of reactant to occur at an appreciable rate. On considering their results and ours the immobilized freedom might be assigned to a translational motion of a molecule.

Figure 10 shows the calculation of the additive effect on the decay (Fig. 5) with the experimental points. The line (c) in Fig. 10 shows the calculation by the use of the initial concentration estimated from the peak height shown in Fig. 6. The calculations using the nominal concentration as the initial concentration failed to reproduce the experimental points. By the addition of ClO_2 the close pairs may convert into the diamagnetic dimers above a certain concentration of ClO_2 even at 77 K. The decrease of the ESR peak-height with addition of ClO_2 shown in Fig. 6 presumably results from the formation of the diamagnetic dimers. Some parameters used in those analyses are summarized in Table 2. In the table r^* is the mean separation of ClO_2 molecules when they uniformly distribute in 3MHX. As ClO_2 added, the

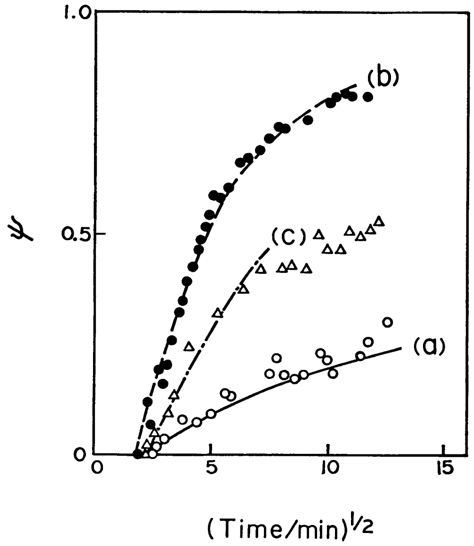

Fig. 10. Additive effect of ClO_2 on its decay in 3MHX at 96 K. The nominal concentration of ClO_2 are at 1.6×10^{-3} (a), 1.1×10^{-2} (b), and 3.5×10^{-2} (c) in units of mol dm^{-3}. The lines show the calculation by use of Eq. 5 in the text. The parameters used in these calculations are shown in Table 2.

TABLE 2. PARAMETERS USED FOR THE SIMULATION OF THE ADDITIVE EFFECT OF ClO_2 ON ITS DECAY IN 3-METHYLHEXANE AT 96 K

Parameter[a)]	$[ClO_2]/10^{-3}$ mol dm^{-3}		
	1.6	11	35
λ	2	2.5	3.33
$R_0/10^{-8}$ cm	10	8	6
$\lambda R_0/10^{-8}$ cm	20	20	20
$D/10^{-15}$ cm^2 min^{-1}	0.11	6.0	5.6
$r^*/10^{-8}$ cm	100	53	36

a) For definition see the text.

values of r^* decrease, but, those of λR_0 are almost constant at 2×10^{-9} m. The difference of the diffusion constants at low and high concentrations may indicate some changes in the properties of the solvent induced by the addition of ClO_2.

As mentioned above, ClO_2 did not decay in supercooled and glassy liquids of toluene and ISB or in polycrystalline heptane. The well-resolved vibrational structure of the electronic absorption spectra of ClO_2 in liquid paraffins disappeared when a hydrogen-bonding solute was added.[13)] Adams reported that the paramagnetic relaxation mechanisms of ClO_2 in hydrogen-bonding or electron-donating solvents, such as alcohols and aromatic hydrocarbons, were different from the mechanisms in paraffin solvents.[14)] He considered that the difference was due to the ClO_2-solvent interaction which was stronger in hydrogen-bonding or electron-donating solvents than in paraffin solvents. On the basis of those studies no decay of ClO_2 in toluene and in ISB might be explained in consideration of the high activation energy arising from the ClO_2-solvent interactions. This speculation is not valid to explain why there is no decay of ClO_2 in heptane. This may result from the fact that heptane is in the polycrystalline state at the temperatures discussed in the present paper.

A few reports mentioned the formation of the ClO_2 dimer.[15,16)] Norman and Porter reported that the electronic absorption spectra of ClO_2 in isopentane-methylcyclohexane rigid solutions were different from the spectra in the liquids.[15)] They considered that the difference of the spectra was due to the formation of the ClO_2 dimer. Nielson and Woltz studied the infrared spectra of gaseous ClO_2.[16)] They speculated that an absorption band at 1.9×10^4 m^{-1} was caused by the dimerization or higher ploymerization of ClO_2. Though those studies do not confirm the presence of a ClO_2 dimer, the reasonable fits of our kinetic analyses suggest that the presence of the ClO_2 dimer is a plausible explanation. To gain additional evidence for the ClO_2 dimer, a study of the optical absorption spectra of ClO_2 in 3MHX around T_g, and some theoretical calculations on the electronic states of ClO_2 and its dimer for assignment of the absorption bands are being planned.

We thank Professor Takahisa Ichikawa for financial assistance in the use of the computers of Hiroshima University.

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