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Solvent Effects on the Photochromic Reactions of Diarylethene Derivatives

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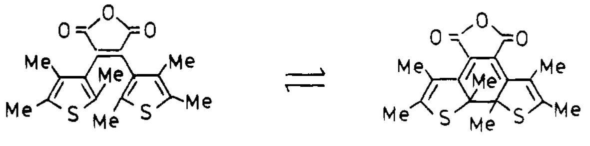
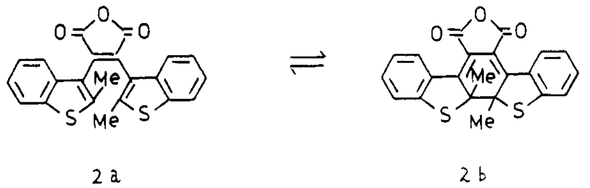
Photochromic reactions of diarylethene derivatives, 1,2-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (**1a**) and 1,2-bis(2-methylbenzothiophene-3-yl)maleic anhydride (**2a**) were found to depend on solvent polarity. The ring-closure quantum yield of **1a** decreased with the increasing solvent polarity from 0.13 in *n*-hexane to 0.003 in acetonitrile. The yield of **2a** decreased from 0.12 in *n*-hexane to 0.03 in acetonitrile. Fluorescence measurement (fluorescence maxima, quantum yields, and decay times) revealed that there existed two kinds of conformations in the excited states, reactive planar and inactive twisted ones, and the state energies for the conformations were dependent on the solvent polarity. The inactive twisted conformation became more stable and dominant in polar solvents, and this explained the low quantum yields. The ring-opening quantum yields were scarcely affected by the solvent polarity.

Introduction

There is an increasing interest in using organic photochromic compounds for rewritable optical memory media.[1-14] Indispensable properties which the compounds should have for this purpose are thermal stability of both isomers and high fatigue resistance, both thermally and photochemically. We have recently developed a new type of thermally stable and fatigue-resistant photochromic compound,[4,7,10,14] diarylethenes with heterocyclic rings, 1,2-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (**1a**) and 1,2-bis(2-methylbenzothiophene-3-yl)maleic anhydride (**2a**).



1a 1b



2a 2b

These compounds have no thermochromicity even at 300 °C, and the colored closed-ring forms are stable for more than 3 months at 80 °C.[8] Furthermore, **2a** was found to have an extremely high photochemical resistance. The cyclization/ring-opening cycles could be repeated more than 10^4 times in benzene while keeping adequate photochromic performance.[8,10] Thus, the diarylethene derivatives are among the most promising photochromic compounds for rewritable optical memory media.

In this report, we have investigated the photochromic reactions of such diarylethenes with heterocyclic rings and electron-withdrawing substituents in various organic solvents and found that the photoinduced ring-closure process as well as fluorescence properties is strongly dependent on solvent polarity. We focused our attention to solve the problem of environmental effects on the reaction pathway in connection with the geometries of the molecules in the excited state.

Experimental Section

1,2-Bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (**1a**) and 1,2-bis(2-methylbenzothiophene-3-yl)maleic anhydride (**2a**) were prepared according to the procedure described before[4,10] and were purified by HPLC (Shimadzu LC-6). The solvents used were spectrograde and purified by distillation before use. All the samples were studied in 1-cm quartz cells and degassed by repeated freeze–pump–thaw cycles. Absorption and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi, U-3410) and a fluorescence spectrophotometer (Hitachi, F-3010), respectively. Fluorescence lifetimes were measured with a time-resolved spectrofluorometer (Horiba, NAES-700L).

A mercury lamp (Ushio, 1 kW) and a xenon lamp (Ushio, 500 W) were used as the light sources. Mercury lines (405 and 546 nm) were isolated by passing the light through a monochromator (Ritsu, MC-10N). The light intensity was measured with a photometer (International Light, IL-700).

Quantum yields of the photochromic reactions, ring closure and ring opening, were determined by comparing the reaction rates with that of **1a** in benzene.[4] Relative fluorescence quantum yields were measured by comparing the intensity with that of **1a** in hexane. Excitation wavelength and the absorbance were fixed at 405 nm and 0.3, respectively.

TABLE I: Spectroscopic Properties of 1a and 1b and Quantum Yields of the Photochromic Reaction

	λ_{max} (nm)		quantum yield[a]		λ_{max} (nm)[b]	
solvent	**1a**	**1b**	**1a** → **1b**	**1b** → **1a**	**1a**	Φ_f[c]
hexane	331	552	0.13	0.16	488	1.0
benzene	340	564	0.07	0.12	541	0.35
THF	335	560	0.04	0.11	560	0.088
CH_3CN	336	563	0.003	0.10		<0.01

[a] **1a** → **1b**: Irradiation with 405-nm light. **1b** → **1a**: Irradiation with 546-nm light. [b] Fluorescence maxima. Excitation wavelength 405 nm. [c] Relative fluorescence quantum yield. Excitation wavelength 405 nm.

Results and Discussion

Photochromism in Various Solvents. Figure 1 shows the photochromic reaction of **1a** in hexane. On exposure to 405-nm light **1a** changed to **1b**, and a new peak appeared at 564 nm (the yellow solution of **1a** turned to red).[4] **1b** returned to **1a** upon irradiation with 546-nm light, and the peak at 564 nm disappeared. (A red color of the solution again returned to yellow.)

The photochromic reaction was found to depend on solvents. The conversion from **1a** to **1b** in the photostationary state under irradiation with 405-nm light decreased with the increasing solvent polarity. The conversion of 73% in hexane decreased to 39% in THF. This indicates that solvent dependence of the ring-closure quantum yield is different from that of the ring-opening yield. Table I summarizes the solvent dependence of the quantum yields. The ring-closure quantum yield in THF was less than one-third of the value in nonpolar hexane. In polar acetonitrile, it was only 0.003. The ring-closure process was strongly suppressed in polar solvents. On the other hand, the ring-opening quantum yields were scarcely affected by the solvent polarity. The quantum yields in benzene, THF, and acetonitrile were almost the same. Solvent

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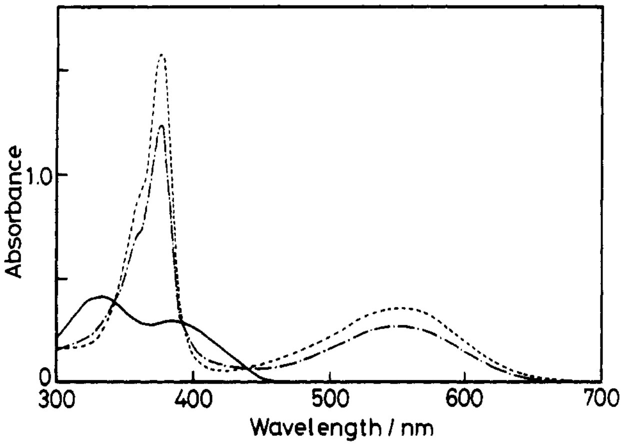

Figure 1. Absorption spectra of **1a** (5.8×10^{-5} mol/L) (—), at the photostationary state under irradiation with 405-nm light (–·–), and **1b** (---).

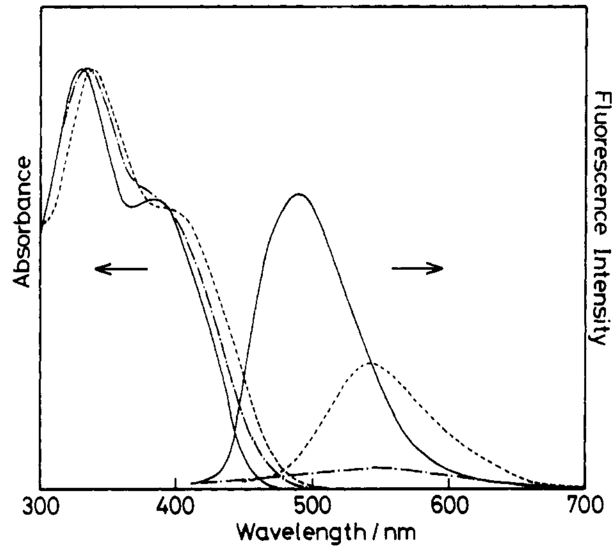

Figure 2. Absorption and fluorescence spectra of **1a** in hexane (—), benzene (---), and THF (–·–).

TABLE II: Spectroscopic Properties of 2a and 2b and Quantum Yields of the Photochromic Reaction

solvent	λ_{max} (nm) **2a**	λ_{max} (nm) **2b**	quantum yield[a] **2a** → **2b**	quantum yield[a] **2b** → **2a**	λ_{max} (nm)[b] **2a**	Φ_f[c]
hexane	407	538	0.12	0.25	487	1.0
benzene	417	541	0.13	0.21	527	1.1
THF	404	533	0.11	0.20	540	0.92
CH_3CN	404	535	0.03	0.19	572	0.058

[a] **2a** → **2b**: Irradiation with 405-nm light. **2b** → **2a**: Irradiation with 546-nm light. [b] Fluorescence maxima. Excitation wavelength 405 nm. [c] Relative fluorescence quantum yield. Excitation wavelength 405 nm.

polarity did not influence the reverse process.

The photochromic reaction of **2a** showed similar solvent dependence. Results are summarized in Table II. The ring-closure quantum yield of 0.12 in hexane decreased to 0.03 in acetonitrile, while the ring-opening quantum yield remained almost constant even the solvent was changed from benzene to acetonitrile.

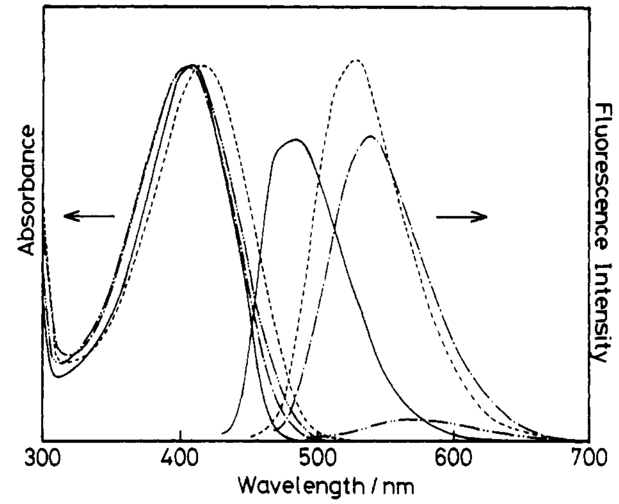

Figure 3. Absorption and fluorescence spectra of **2a** in hexane (—), benzene (---), THF (–·–), and acetonitrile (–··–).

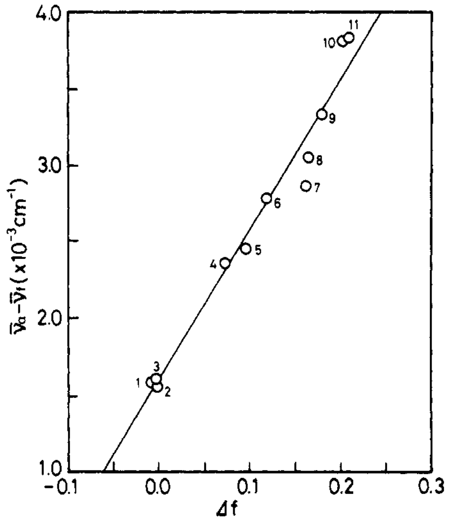

Figure 4. Plots of $(\nu_a - \nu_f)$ of **1a** vs Δf: 1, cyclohexane; 2, *n*-heptane; 3, *n*-hexane; 4, diphenyl ether; 5, di-*n*-butyl ether; 6, di-*n*-propyl ether; 7, diethyl ether; 8, *tert*-butyl methyl ether; 9, diethylene glycol diethyl ether; 10, ethyl acetate; 11, THF. $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$.

Absorption and Fluorescence Spectra. Figure 2 shows the absorption and fluorescence spectra of **1a** in various solvents. Table I summarizes the maxima of the open-ring and closed-ring forms. Absorption maxima of the open-ring form in benzene, THF, and acetonitrile were observed in the wavelengths ranging from 335 to 340 nm. Although the maximum showed a small hypsochromic shift in hexane, the solvent shift in the absorption spectrum was rather small. On the other hand, the fluorescence spectra showed remarkable Stokes shifts depending on the solvent polarity. The maximum at 488 nm in hexane shifted to 560 nm in THF. At the same time, the intensity decreased. The fluorescence intensity in acetonitrile was less than 1% of the intensity in hexane. The results indicate that the excited state of the open-ring form has a polar structure with a large dipole moment. The absorption maximum of the closed-ring form **1b** remained in the wavelengths ranging from 560 to 564 nm even when the solvent was changed from benzene to acetonitrile.

Although similar solvent effect was observed for compound **2a**, the Stokes shifts of the fluorescence maxima and the intensity changes were smaller than those observed for **1a**, as shown in Figure 3 and Table II. The fluorescence of **2a** had the maximum intensity in bezene. The intensity decreased, when the solvent polarity was further increased from benzene to acetonitrile. In acetonitrile, the intensity was less than 6% of the intensity in hexane, though the intensity was much higher than that observed for **1a**.

Excited-State Properties. As described above, the fluorescence spectra showed large Stokes shifts depending on the solvent polarity. We attempted to evaluate the excited-state dipole moment by applying the Lippert–Mataga equation.[15,16]

The fluorescence spectra of **1a** were measured in 11 solvents. Figure 4 shows the Lippert–Mataga plot. The increase of $\nu_a - \nu_f$ with increasing Δf (= $[(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$) indicates that the excited state has a larger dipole moment

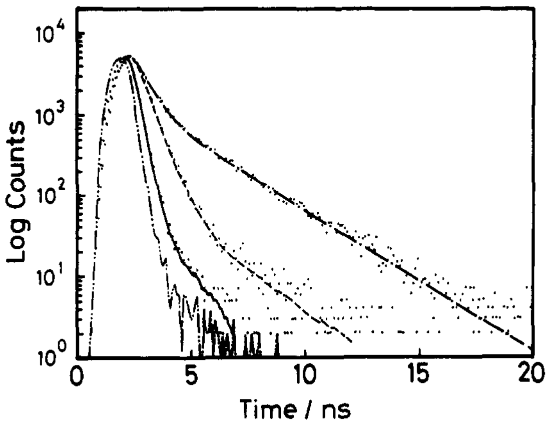

Figure 5. Fluorescence decay curves of **1a** in hexane (—), benzene (– – –), and THF (–·–); light pulse shape (–··–). λ_{ex} = 404 nm; λ_{em} = 460 ± 10 nm in hexane, 500 ± 10 nm in benzene, and 520 ± 10 nm in THF.

TABLE III: Fluorescence Decay Time of 1a

solvent	τ_{f1}, ns	τ_{f2}, ns	A_{f1}/A_{f2}
hexane	0.34	1.10	98/2
benzene	0.54	2.40	97/3
THF	0.62	2.47	57/43

than the ground state. The difference between the ground and the excited states, $\mu_e - \mu_g$, was calculated to be 1.0 × $10^{12}a_0^{3/2}$ cm$^{-3/2}$ D from the slope, where a_0 is the Onsager cavity radius. If we assume a_0 as 6.0 × 10^{-8} cm,[17] the difference is estimated to be 15 D. The large difference indicates that the molecule in the excited state has an extremely polar structure.

Figure 5 shows fluorescence decay curves of **1a** in various solvents. The decay curves could be analyzed by a two-component model, in which interconversion of the two components is negligible and both decay exponentially. Table III summarizes the relative contribution of the two components and their decay times. The contribution of the slower decaying component increased with the increasing solvent polarity. The solvent dependence implies that the slower decaying component is the emission from the more polar excited state.

Mechanism of the Photochromism. Compounds **1a** and **2a** showed large Stokes shifts in polar solvents. Such large Stokes shifts have been observed in many TICT (twisted intramolecular charge transfer) molecules.[18] These molecules have both an electron donor group and an acceptor one within the molecule. In polar solvents, excitation brings about intramolecular electron transfer from the donor to the acceptor and results in charge-separated polarized states, in which the donor and the acceptor groups are in a perpendicular geometry.

The TICT state is characterized by a dual-fluorescence spectrum, a bathochromic shift of the fluorescence band with increasing solvent polarity, and low fluorescence intensity in polar solvents. Compounds **1a** and **2a** showed large bathochromic shifts of the fluorescence spectra, and the fluorescence yields decreased in polar solvents. Fluorescence decay time measurement indicated that there existed two kinds of excited states, fast and slower decaying components, and the latter was the emission from the more polar state. It is inferred from these results that **1a** and **2a** have TICT characters in the excited states.

Actually, **1a** consists of two thiophene rings and a maleic anhydride moiety; the former is a donor and the latter an acceptor. **2a** has two benzothiophene rings as the electron donating group. According to the general consideration of the TICT molecules,[18-22] **1a** is considered to change its conformation by the rotation of the single bond between the thiophene ring and the maleic anhydride in the excited state, depending on the solvent polarity, as shown in Figure 6. In less polar solvents, a planar less polar conformation is energetically more stable than twisted polar one. In polar solvents, however, the twisted charge transfer state becomes more stable than the planar state. Decrease of the ring-closure quantum yields in polar solvents implies that the TICT state is not responsible for the photochromic reaction, and the interconversion between the TICT state and the planar geometry state is not possible.

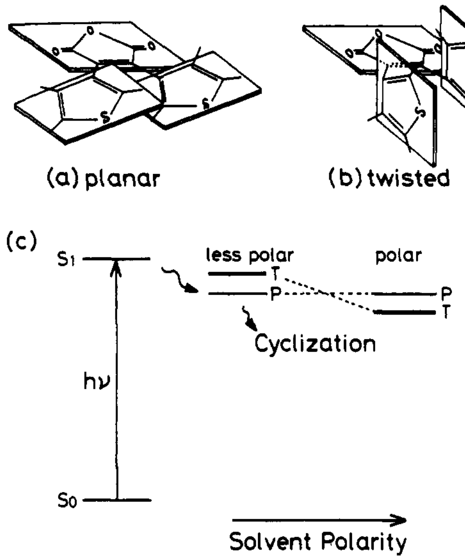

Figure 6. Schematic illustration of solvent effects. (a) The planar form and (b) the twisted form of **1a** in the excited state. (c) Excited states in various solvent polarity. P and T denote the planar and twisted forms, respectively.

The ring-closure reaction of **1a** is considered to proceed as follows (Figure 6). The Franck–Condon state conformation of the molecule is in between planar and perpendicular geometries. In less polar solvents, the excited state stabilizes to a planar conformation with a low dipole moment and undergoes a concerted ring-closure reaction in the conrotatory mode.[23] The planar geometry is close to the structure of the closed-ring form. In polar solvents, on the other hand, the Franck–Condon state converts to the energetically more stable charge-separated state. This state with a large dipole moment undergoes a twist which forces the plane of a thiophene ring to become perpendicular to that of the maleic anhydride moiety. The perpendicular geometry is disadvantageous to the ring-closure reaction and deactivates to the ground state without any reaction. In this geometry, the two moieties are orbitally decoupled, and the radiative transition from the excited state to the ground state is overlap forbidden. The low fluorescence yields and the longer decay time in polar solvents are thus expected. The interconversion between the twisted and planar conformations is considered to be negligible, because photocyclization was scarcely observed in polar solvents and the decay time of the fast decaying component in THF was longer than the time in hexane. The two states are separated each other by some energy barrier.[24]

A similar mechanism is applicable to **2a**. In less polar solvents, the twisted conformation has higher energy level than the planar conformation, so that the ring-closure reaction proceeds easily. As the solvent polarity increases, the energy level of the twisted conformation comes close to that of the planar conformation. The weaker donor ability of the benzothienyl group in comparison with the thienyl group, however, cannot further stabilize the charge-transfer state below the state of the coplanar conformation. Thus, even in very polar solvents such as acetonitrile, the ring-closure reaction proceeds to a certain extent. Solvent dependence of the reaction was not observed for 1,2-bis(2-methylbenzothiophene-3-yl)perfluorocyclopentene,[14] in which the acid anhydride moiety was replaced with perfluorocyclopentene.

Conclusion

Photochromic reactions of diarylethene derivatives **1a** and **2a** were found to depend on the solvent polarity. The ring-closure quantum yields decreased with increasing solvent polarity, while the ring-opening quantum yields were scarcely affected by the solvents. Fluorescence measurements revealed that stabilization of the TICT states in the excited states in polar solvents shifted the fluorescence maxima to longer wavelengths, decreased the fluorescence yields, and increased the fluorescence decay time. The increase of the contribution of the TICT state in the excited state decreased the ring-closure quantum yield.

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Heterogeneous Interactions of $ClONO_2$ and HCl on Nitric Acid Trihydrate at 202 K

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Using a low-pressure flow tube coupled to a mass spectrometer, reaction probabilities (γ's) for $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ (1) and $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ (2) have been measured on nitric acid trihydrate (NAT) films at 202 K for reactant partial pressures in the 10^{-6} Torr range. When the water vapor pressure over the NAT film approaches that of ice ($P_{H_2O} \approx 1.5 \times 10^{-3}$ Torr, H_2O-rich NAT), $\gamma_1 = 0.002 \pm 0.001$ and $\gamma_2 > 0.2$. For lower water partial pressures ($P_{H_2O} \approx 2 \times 10^{-4}$ Torr), characteristic of HNO_3-rich NAT, the γ's decrease by 2 orders of magnitude. For HCl partial pressures of 5×10^{-6} Torr, the experiments indicate that H_2O-rich NAT films take up HCl in amounts similar to those taken up by water-ice surfaces ($\approx 1 \times 10^{15}$ molecules/cm^2); HNO_3-rich NAT films take up 2 orders of magnitude less HCl ($< 1 \times 10^{13}$ molecules/cm^2). At high HCl partial pressures ($> 1 \times 10^{-4}$ Torr), very much greater uptake by both H_2O-rich and HNO_3-rich films is observed, indicating that the NAT films melt under these conditions.

Introduction

Reactions between reservoir chlorine species on the surfaces of polar stratospheric clouds (PSCs) are now widely believed to be instrumental in the springtime loss of ozone which occurs at polar latitudes. Reactions such as (1) and (2) convert chlorine

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (1)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (2)$$

from the reservoir species $ClONO_2$ and HCl over to Cl_2 and HOCl, which photolyze readily and form chlorine-containing free radicals capable of destroying ozone.[1-3] The polar stratospheric clouds which act as catalysts for these reactions are believed to be composed of either nitric acid trihydrate (type I PSC) or water-ice (type II PSC). The type I PSCs are more prevalent because the frost point for nitric acid trihydrate (NAT) is higher than that of water-ice.

The kinetics of these reactions on solid surfaces of composition similar to the PSCs have been studied by several groups. Molina et al.,[4] Tolbert et al.,[5] and Leu[6] reported that reactions 1 and 2 proceed readily on cold water-ice surfaces. Studies on frozen mixtures of HNO_3 and H_2O by Tolbert et al.,[5], Moore et al.,[7] and Leu et al.[8] showed that the observed reactivity can be a strong function of the specific composition of the HNO_3-doped ice. More recently, Hanson and Ravishankara[9] have shown that these processes occur readily at stratospheric partial pressures of $ClONO_2$ and HCl on both water ice films and on thin NAT films in coexistence with water-ice.

Our understanding of the physical chemistry of these solid substrates has also improved since the discovery of the ozone hole. The thermodynamically stable form of NAT in the stratosphere is determined by the ambient conditions: at a given temperature, fixing the H_2O vapor pressure determines the HNO_3 vapor pressure and hence the composition of the surface layers of the NAT solid.[10,11] When the H_2O pressure approaches that of ice, we refer to the NAT solid as "H_2O-rich" and when it approaches values characteristic of the coexistence between NAT and nitric acid monohydrate, we refer to it as "HNO_3-rich". Abbatt and Molina[12] have shown that there is a large variation in the reaction probability (γ) between these two types of NAT for the reaction of HOCl with HCl.

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