The Thermal Reactions of Azido-1,3,5-triazines

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Azido-*s*-triazines containing –Cl, –OCH$_3$, and –N(CH$_3$)$_2$ groups were synthesized, and their thermal reactions with some hydrocarbons were investigated with respect to the reaction products and the reaction kinetics. With non-olefinic hydrocarbons the reactions were found to proceed *via* a nitrene intermediate; in the reactions with cyclohexane, cyclohexylamino-*s*-triazines and amino-*s*-triazines were obtained. On the other hand, with olefinic hydrocarbons the reactions took place *via* a bimolecular mechanism involving a formation of an intermediate of the triazoline type; in the reactions with cyclohexene, cyclohexenylamino-*s*-triazines were obtained along with amino-*s*-triazines. In both cases, the yields of alkylamino and alkenylamino-*s*-triazines increased with the electron-withdrawing power of the substituents in the *s*-triazine nucleus.

There have been a number of studies of the thermal and photochemical reactions of azido compounds;[1] in recent years the reactions and structures of azido derivatives of nitrogen heteroaromatics such as pyridine,[2,3] pyridazine,[4] pyrimidine,[5–8] pyrazine,[9,10] quinoline,[11] and acridine[12] have been investigated.

Azido-*s*-triazines have been known for a long time; however, little is known about their reactions. In the reactions of azido-*s*-triazines with such nucleophiles as sodium hydroxide[13] and ammonia,[14] the azido group is replaced by hydroxy and amino groups, while some azido-*s*-triazines are known to decompose violently on heating.[13,15] Recently, the presence of a nitrene intermediate was confirmed in the photolysis of azido-*s*-triazine,[16] and amino-*s*-triazines were obtained from azido-*s*-triazines upon irradiation in methanol.[17] However, the details of the thermal and photochemical reactions of azido-*s*-triazines have not yet been revealed. On the other hand, the thermolysis and photolysis of azido-*s*-triazines may provide useful and convenient routes for the preparation of a number of *s*-triazine derivatives which would otherwise be difficult to synthesize. This paper will report on the thermal reactions of azido-*s*-triazines with several hydrocarbons.

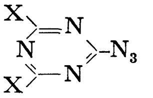
Results and Discussion

*Syntheses of Azido-*s*-triazines.* Azido-*s*-triazines containing –Cl, –OCH$_3$, and –N(CH$_3$)$_2$ groups in the *s*-triazine nucleus were prepared by the condensation of the corresponding chloro-*s*-triazines with sodium azide. Table 1 lists the compounds thus obtained. These monoazido-*s*-triazines are thermally-stable compounds. Compound **1** is distillable, while Compound **2** can be sublimed under reduced pressure; all of them decomposed at about 200 °C, showing no significant substituent effect upon their thermal stabilities.

*Structure of Azido-*s*-triazines.* It is well known that an azidoazomethine-tetrazole equilibrium exists in 2-azido-nitrogen heteroaromatics; the position of the equilibrium is known to depend upon the solvent, the temperature, and the electronegativity of the heterocyclic ring. Generally, the electron-withdrawing ability of the heterocyclic ring is considered to stabilize the azido form;[18] azido-pyridines exist in equilibrium with the tetrazole form, but the equilibrium lies strongly on the side of the tetrazole,[19] and azido-pyrimidines exist in both the azido and tetrazole forms, while 2-amino-4,6-diazido-*s*-triazine is known to exist in the diazido form.[20]

The IR spectra of these azido-*s*-triazines in KBr discs have a strong and sharp characteristic band near 2100 cm^{-1} assignable to the azido group, suggesting that these compounds exist in the azido form in a solid state. In addition, the PMR spectra of Compounds **2** and **3** in CCl$_4$, CDCl$_3$, DMSO-d_6, and CF$_3$COOH at 40 and 60 °C showed a signal assignable to –OCH$_3$ or –N(CH$_3$)$_2$ as a singlet in every case in spite of the wide diversity in the nature of the solvent (see Table 2), indicating the absence of tautomeric tetrazole, which should possess two kinds of methoxy or dimethylamino groups respectively; azido-*s*-triazines containing ordinary substituents in the *s*-triazine nucleus exist in the azido form not only in a solid state, but also in a solution, regardless of the solvent employed. The fact that the azido form is the sole species in Compound **3**

Table 1. 4,6-Disubstituted 2-azido-*s*-triazines



No.	Substituent	Mp (°C)	Decomp. (°C)	Solvent for recrystallization	Anal. (%) Found C	H	Cl	Cacld C	H	Cl
1	Cl	60—61 (85)[a]	205	Ligroin	—	—	37.41	—	—	37.12
2	OCH$_3$	85—85.5	195	Benzene–Ligroin	32.62	3.64	—	32.97	3.32	—
3	N(CH$_3$)$_2$	106—107	205	Methanol	39.99	6.10	—	40.37	5.81	—

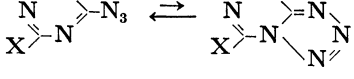
a) C. Hart, *J. Amer. Chem. Soc.*, 1922 (1928).

Table 2. PMR data of 2-azido-4,6-dimethoxy-*s*-triazine (**2**) and 2-azido-4,6-bis(dimethylamino)-*s*-triazine (**3**)

Solvent	Chemical shifts (δ)[a]	
	2	**3**
CCl_4	4.00	3.11
$CDCl_3$	4.05	3.13
DMSO-d_6	3.98	3.07
CF_3COOH	4.40	3.37

a) TMS was used as the internal standard.

[the bis(dimethylamino)-*s*-triazinyl group is known to be the least electron-attracting group among the common *s*-triazinyl groups][21] suggests that the presence of three ring nitrogen atoms in the heterocyclic nucleus is sufficient for the electron-withdrawing power of the heterocycle to shift the azidoazomethine-tetrazole equilibrium far to the left, regardless of the substituents in the heterocycle.

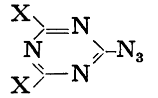


X = -Cl, $-OCH_3$, $-N(CH_3)_2$

*Reactions of Azido-*s*-triazines with Hydrocarbons.* It is known that acyl azides, such as azido formates and sulfonyl azides, decompose thermally or photochemically to give the corresponding nitrenes, which then react with aliphatic hydrocarbons to give alkylamino derivatives as the insertion products. On the other hand, it is known that, in the thermal reactions with aliphatic hydrocarbons, ordinary aryl azides do not afford the corresponding nitrene insertion products as the major products. Recently, it was reported that, in the reaction of phenyl azide with cyclohexane, *N*-cyclohexylaniline was obtained with aniline.[22] The situation of the *s*-triazinyl group as a aromatic group is of interest because of its strong electron-attracting character.

When the azido-*s*-triazines were heated in cyclohexane at 180—190 °C under pressure, the corresponding amino-*s*-triazines and cyclohexylamino-*s*-triazines were obtained as the major products in every case. Table 3 lists the yields of these *s*-triazine derivatives.

Table 3. Yields of amino- and cyclohexylamino-*s*-triazines in the reactions of azido-*s*-triazines with cyclohexane at 190 °C



Azido-*s*-triazine	Substituent X	Yields (%)	
		Amino-*s*-triazine	Cyclohexylamino-*s*-triazine
1	Cl	—	23<[a]
2	OCH_3	15	22
3	$N(CH_3)_2$	17	trace

a) Isolated after methoxydechlorination.

In the case of Compound **1**, because of the presence of active chlorine atoms in the *s*-triazine nucleus, the formation of a large quantity of a metal-containing decomposition product (the metallic constituents of the by-products are considered to result from the autoclave used) was observed. Therefore, the yields of the major reaction products should increase in the reactions in inert reactors.

From Table 3 it is obvious that the substituents in the *s*-triazine nucleus considerably affect the yields of the products; it can be said that the electron-withdrawing substituents in the *s*-triazine nucleus favor the formation of cyclohexylamino-*s*-triazine and that, in the thermal reactions of aryl azides with aliphatic hydrocarbons, the yields of the alkylamino derivatives become higher with an increase in the acidic character of the aryl group.

On the other hand, when azido-*s*-triazines were heated in cyclohexene under pressure at 180—190 °C, the corresponding amino-*s*-triazines and cyclohexenylamino-*s*-triazines were obtained in every case, as is shown below.

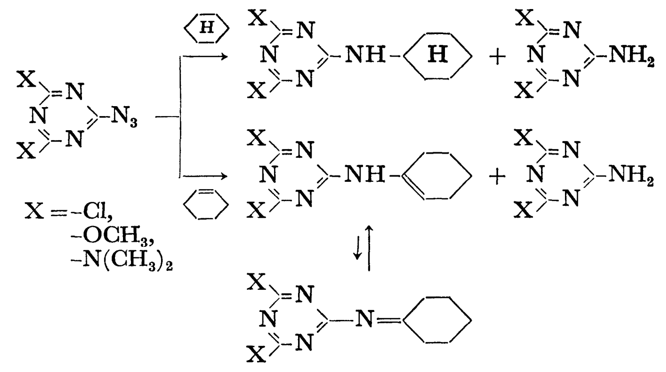
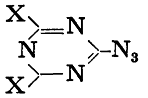


Table 4 lists the yields of the amino- and cyclohexenylamino-*s*-triazines thus obtained. In the reaction of Compound **1** with cyclohexene, the formation of a large quantity of metal containing decomposition product was also observed.

From the concept[23] generally accepted for the structure of ordinary enamines possessing a secondary nitrogen atom, the tautomeric equilibrium between enamine and imino forms in *s*-triazinyl enamines can be expected

Table 4. Yields of amino- and cyclohexeneylamino-*s*-triazines in the reactions of azido-*s*-triazines with cyclohexene at 190 °C



Azido-*s*-triazine	Substituent X	Yields (%)	
		Amino-*s*-triazine	Cyclohexenylamino-*s*-triazine
1	Cl	—	22<[a]
2	OCH_3	16	44
3	$N(CH_3)_2$	17	—

a) Isolated after methoxydechlorination.

Table 5. PMR data of 2-(cyclohexene-1-ylamino)-4,6-dimethoxy-*s*-triazine

Solvent	Chemical shifts (δ)[a]			
	$-(CH_2)_4-$(m)[b]	CH_3O-(s)[b]	=CH–(m)[b]	–NH–(b)[b]
CCl_4	1.50—2.50 (8)[c]	3.88 (6)[c]	5.93 (1)[c]	7.40 (1)[c]
$CDCl_3$	1.30—2.50 (8)	3.91 (6)	6.05 (1)	6.95 (1)
DMSO-d_6	1.43—2.43 (8)	3.87 (6)	5.96 (1)	8.91 (1)

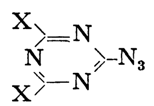
a) TMS was used as the internal standard. b) m: multiplet, s: singlet, b: broad. c) Indicates the number of protons.

to lie far to the side of the imino form. However, in the PMR spectra of cyclohexenylamino-*s*-triazines, the presence of NH and olefinic protons was observed in a ratio of 1: 1, as is shown in the case of the dimethoxy-*s*-triazine derivative (see Table 5). This fact indicates that the cyclohexenylamino-*s*-triazine exists as the enamine form, suggesting that the strong electron-attracting character of the *s*-triazinyl group prevents the overlap of the lone pair of electrons on the –NH– nitrogen with the π electrons of the enaminic double bond, and that the N→C migration of the NH proton to form the imino form becomes difficult; in ordinary *s*-triazine derivatives the enamine form may be the stable one, as in the cases of *N*-acyl vinylamines[24] and *N*-ethoxycarbonylcyclohexenylamine.[25]

*Kinetics of the Reactions of Azido-*s*-triazines with Hydrocarbons.* As has been described above, azido-*s*-triazines react thermally with cyclohexane and cyclohexene to give the insertion and abstraction products of the nitrenes corresponding in appearance. Thus, in order to make clear the progress of the reactions of azido-*s*-triazines with these hydrocarbons, kinetic measurements of the reactions were carried out.

When azido-*s*-triazines were heated in hydrocarbons, an evolution of nitrogen was observed in every case. Therefore, for the kinetic measurements, an increase in the volume of nitrogen evolved was followed with the lapse of time in various substrates. Since a plot of ln $V_\infty/V_\infty - V_t$ (where V_t and V_∞ are the volumes of nitrogen evolved at time t and at an infinite time respectively) against the reaction time, t, was found to give a straight line up to about a 90% conversion of the azido-*s*-triazines, as is shown in Fig. 1, the first-order rate constants for the decomposition of azido-*s*-triazines were calculated from the slopes of the straight lines; they are listed in Table 6.

Table 6. Rate constants for the decomposition of azido-*s*-triazines in various substrates at 184.3 °C



Substrate		$k_1 \times 10_1$ (s^{-1})		
	X=	–Cl	$-OCH_3$	$-N(CH_3)_2$
Cyclohexane		—	2.88	—
Decalin		3.07	2.36	3.38
Tetralin		2.30	2.21	3.04
Diphenyl ether		—	1.83	3.42
Acetophenone		—	2.06	4.39
Dimethyl terephthalate[a]		—	1.94	—
Cyclohexene		b)	66.9	20.9
1-Tetradecene		b)	61.0	33.7
Methyl oleate		31.9	26.1	12.0
Diethyl maleate		70.2	59.4	82.0

a) measured with 43.5% Decalin solution b) Rate constant was too fast to measure.

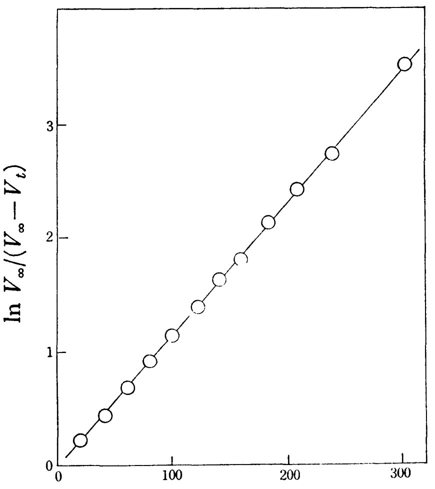


Fig. 1. Decomposition of 2-azido-4,6-dimethoxy-*s*-triazine in acetophenone at 184.3 °C.

From Table 6 it is obvious that, in the reactions with cyclohexane, decalin, tetralin, diphenyl ether, and dimethyl terephthalate, there was little variation in the rate in spite of the wide diversity in the nature of the substrates, suggesting that the rate-determining step of these reactions is the loss of nitrogen and the formation of an electron-deficient nitrene species. The substrates were assumed to participate merely as solvents. For a detailed discussion of the reactions of azido-*s*-

Table 7. Rate constants for the decomposition of 2-azido-4,6-dimethoxy-*s*-triazine at various temperatures

Temp. (°C)	$k_1 \times 10_4$ (s^{-1})		
	Decalin	Cyclo-hexene	Methyl oleate
154.0	—	—	6.48
164.2	—	22.7	11.0
174.2	0.96	39.7	15.6
184.3	2.36	66.9	26.1
194.0	5.45	—	—

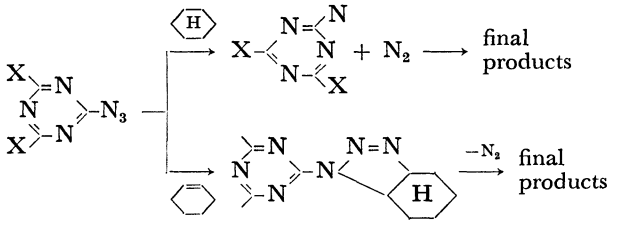
Table 8. Activation parameters for the decomposition of 2-azido-4,6-dimethoxy-*s*-triazine

Substrate	$\Delta H^{\neq}$ (kcal·mol^{-1})	$\Delta S^{\neq}$ (184.3 °C) (cal·deg^{-1}·mol^{-1})
Decalin	36.7	+4
Cyclohexene	21.0	−23
Methyl oleate	16.8	−34

triazines with these substrates, the temperature dependence of the reaction constant for the decomposition of Compound **2** was measured in decalin; the results are listed in Table 7. From these values, the activation parameters for the reaction were calculated; they are shown in Table 8.

The entropy of activation of +4.0, which is comparable in magnitude to those of the reactions of sulfonyl azides with similar substrates, suggests that the reaction is of the first order involving the nitrene intermediate;[26] it can be generally said that the thermal reactions of azido-*s*-triazines with non-olefinic hydrocarbons proceed *via* a nitrene intermediate.

On the other hand, in the reactions of azido-*s*-triazines with olefinic hydrocarbons, the situation was different from that described above. For example, the rate constants for the reactions of Compound 2 with cyclohexene, 1-tetradecene, methyl oleate, and dimethyl maleate were larger than those for the reactions with non-olefinic substrates and (see Table 5) differed significantly from each other, suggesting that the rate-determining step of these reactions is not the loss of nitrogen from azido-*s*-triazines. Moreover, the entropies of activation were of a large negative value, as is shown in Table 8. Therefore, it is unlikely that the decomposition of azido-*s*-triazines in olefinic hydrocarbons proceeds *via* a nitrene intermediate; it may be reasonable to consider that the reactions of azido-*s*-triazines with olefins take place *via* a bimolecular mechanism involving an intermediate of the triazoline type which decomposes rapidly under the cleavage of the nitrogen to give the final products.[27]



If this reaction process is correct, the amino-*s*-triazines in the reactions with olefins should result from the triazoline intermediates or cyclohexenylamino-*s*-triazines.

When Compound 2 was heated at 120 °C in cyclohexane for 40 hr, merely 5% of the azide was decomposed, forming amino-*s*-triazine in a yield of 6% of the decomposed azide. However, when Compound 2 was heated in cyclohexene at 120 °C for 30 hr, all of the azide was decomposed to yield cyclohexenylamino-*s*-triazines in a yield of 34% and amino-*s*-triazine in a yield of 26%. In addition, the cyclohexenylamino-*s*-triazines gave the corresponding amino-*s*-triazines in good yields upon heating in olefinic substrates under similar reaction conditions, suggesting that the amino-*s*-triazines in the reactions of azido-*s*-triazines with olefins did not result from the nitrene intermediates, but, rather, from the cyclohexenylamino-*s*-triazines. Details of the decomposition of cyclohexenylamino-*s*-triazines are now being studied and will be reported elsewhere.

Experimental

All the melting points are uncorrected.

The infrared spectra were measured in potassium bromide discs on a Jasco D-301 spectrometer. The NMR spectra were recorded on a Varian A-60D spectrometer. The ultraviolet spectra were recorded on a Hitachi-124 UV-VIS spectrometer. The elemental analyses were performed in the Micro-analytical Center of Gunma University.

The identification of the reaction products was performed by means of studying their NMR and infrared spectra, by elemental analyses, by a molecular-weight determination, and by a mixed-melting-point test with an authentic sample.

Materials. A typical preparation is shown in the case of Compound **2**. A solution of 7.5 g (0.115 mol) of sodium azide in 80 ml of water was stirred, drop by drop, into a solution of 13.5 g (0.075 mol) of 2-chloro-4,6-dimethoxy-*s*-triazine in 100 ml of acetone at 40 °C. After stirring for 4 hr at 40 °C, the reaction mixture was poured into 300 ml of ice-water. The precipitate was then filtered and dried to give 9.5 g (84%) of a crude product. The recrystallization of the product from benzene–ligroin gave an analytical sample of Compound **2**. Mp 85—85.5 °C. IR (KBr) cm^{-1}: (N_3) 2140 and (*s*-triazine) 810. DTA: 85 °C (endothermic) and 195 °C (exothermic).

*Reactions of Azido-*s*-triazines with Cyclohexane.* Typical examples will be shown in the cases of Compounds **1** and **2**.

1) A solution of 7.0 g (0.037 mol) of Compound 1 in 50 ml of cyclohexane was heated for 7 hr at 180—190 °C in an autoclave. After the solvent had then been evaporated *in vacuo*, the residue was treated with a solution of 5.4 g (0.1 mol) of sodium methoxide in 50 ml of methanol for 12 hr at room temperature. After the insoluble matter had been filtered off, the solution was evaporated *in vacuo*. From the benzene extract of the residue, 2-cyclohexylamino-4,6-dimethoxy-*s*-triazine was obtained in a yield of 23%; mp 123.5—125.5 °C (methanol–water).

2) A solution of 5.0 g (0.026 mol) of Compound **2** in 50 ml of cyclohexane was heated for 7 hr at 180—190 °C in an autoclave. After the reaction mixture had then been cooled to room temperature, the crystal was filtered to give 0.7 g (yield, 16%) of 2-amino-4,6-dimethoxy-*s*-triazine; mp 214—216 °C (lit,[28] 219 °C). The filtrate was evaporated in vacuo; then the residue was purified by silica gel column chromatography [developing solvent, benzene: acetone = 100: 5 by volume] to give 1.5 g (yield 22%) of 2-cyclohexylamino-4,6-dimethoxy-*s*-triazine; mp 127—128 °C (lit,[28] 127—129 °C).

In the reaction of Compound **3** with cyclohexane 2-amino-4,6-bis(dimethylamino)-*s*-triazine (yield, 17%) dioxane (mp 221—222 °C) (lit,[29] 222 °C) was obtained along with a small amount of 2-cyclohexylamino-4,6-bis(dimethylamino)-*s*-triazine.

*Cyclohexylamino-*s*-triazines.* A typical preparation of an authentic sample of cyclohexylamino-*s*-triazine is shown below in the case of 2-cyclohexylamino-4,6-bis(dimethylamino)-*s*-triazine. A solution of 2.0 g (0.01 mol) of 2-chloro-4,6-bis(dimethylamino)-*s*-triazine in 30 mol of cyclohexylamine was refluxed for 8 hr, and then the mixture was poured into 300 ml of ice–water. After the mixture had then been neutralized with hydrochloric acid, the crystal was filtered and dried. Recrystallization from petroleum ether gave 1.3 g of an analytical sample of 2-cyclohexylamino-4,6-bis(dimethylamino)-*s*-triazine. Mp 68—69 °C. Found: C, 58.79; H, 9.40%. Calcd for $C_{13}H_{24}N_6$: C, 59.06; H, 9.15%.

*Reaction of Azido-*s*-triazines with Cyclohexene.* A typical example is shown in the case of Compound 2.

A solution of 20.0 g (0.11 mol) of Compound 2 in 200 ml of cyclohexene was heated for 7 hr at 180—190 °C in an autoclave. After the reaction mixture had then been cooled to room temperature, the crystals were filtered off to give 2.0 g (yield, 12%) of 2-amino-4,6-dimethoxy-*s*-triazine; mp 215—216 °C (lit,[28] 219 °C). From the filtrate, 13.0 g of 2-(cyclohexene-1-ylamino)-4,6-dimethoxy-*s*-triazine were obtained as a crystalline precipitate after cooling for 1 night at 0 °C. Mp 92—93 °C (Ligroin). Found: C, 56.14; H, 7.03; N, 23.47%. Calcd for $C_{11}H_{16}N_4O_2$: C, 55.91; H, 6.83; N, 23.72%. Mass: $m/e=236$. IR, cm^{-1}: (NH) 3150, (C=C) 1670, and (*s*-triazine) 815.

The compound absorbed 1 mol of bromine in chloroform and was oxidized by potassium permanganate in pyridine at room temperature.

Kinetic Measurements. The kinetic measurements were carried out by following the increase in the volume of nitrogen evolved or the decrease in the intensity of the N_3 band of azido-*s*-triazine [Compound **1**=2140 cm^{-1}: Compound **2**=2160 cm^{-1}; Compound **3**=2125 cm^{-1}].

The nitrogen evolation rates were measured by the methods of Overberger[30] and Leffler.[31] 40 ml of a substrate in a 100 ml long-necked flask was immersed in a constant-temperature bath controlled to ±0.1 °C using polyethylene glycol and then allowed to reach the equilibrium temperature and pressure.

A weighed amount of the azide, 0.002—0.003 mol in 10 ml of the substrate, was poured into the flask. The flask was connected to the azotometer through a small condenser and a stopcock, and the reading of the volume was adjusted to zero. The stopcock was then closed, the solution was shaken well, and the measurement was started. The volume change in the nitrogen was followed for 90% of the reaction. The infinity volume of gas was determined by the reading after no increase in gas volume was observed (after about 6—7 hr).

In the reactions with cyclohexane, cyclohexene, and diethyl maleate, the kinetic runs were carried out by measuring the decrease in the intensity of the N_3 band.[32] A typical run is shown below in the reaction of Compound **2** with cyclohexane. A solution of Compound **2** in cyclohexane (0.14 mol/l) was heated in a constant-temperature bath in about 20 small glass sealed tubes 12 cm in length and 8 mm in diameter. At intervals of about 10 min the tubes were poured into cold water to stop the reaction, and the IR spectra of the solutions were measured. The first-order rate constant for the decomposition of the azido-*s*-triazine was calculated using Eq. (1):

$$k_1 t = -\ln [\log (T_\infty/T_0)/\log (T_\infty/T_t)] \qquad (1)$$

where T_∞, T_t, and T_0 represent the transmittances at an infinite time, at time t, and at time zero respectively.

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