Similarly, the fluorescence quenchings of riboflavin were treated by eq. (1) to obtain the K_c values. As seen in Table I, the K_c values determined by fluorescence quenching agree very closely with those determined by absorption change, indicating a static quenching[8] of the riboflavin fluorescence by the phenothiazines. Although the experimental temperature in spectral studies was different from that in kinetic studies, it is interesting to note that the larger the K_c values, the greater the extent of photolysis was generally observed. It is well known that riboflavin is a good electron acceptor and phenothiazine derivatives are good electron donor.[9] Thus, the formation of charge-transfer complex between riboflavin and tranquilizing phenothiazine as an intermediate[10] in ground state and/or in excited state may play an important role in the present photolysis, although various mechanisms[2,4] have been proposed for riboflavin-sensitized photooxidation.

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Use of a Macroreticular Resin Containing Isothiocyanate Group as Insoluble Reagent. Removal of Primary and Secondary Amines

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A macroreticular resin containing isothiocyanate group was proposed as an insoluble reagent and applied to the removal of the primary and secondary amines. The reaction condition of this resin with primary and secondary amines were determined. Most of the aliphatic amines tested, except for primary amines having tertiary alkyl group, were retained on the resin by shaking at 50° for 2 hr. Three kinds of impurities in commercial triethylamine could be removed by using this resin.

Keywords——macroreticular isothiocyanate resin; insoluble reagent; removal of primary and secondary amines; reactivity of isothiocyanate resin with amines; removal of impurities in triethylamine

3-Nitrophthalic acid anhydride, *p*-toluene sulfonyl chloride, and phenyl isothiocyanate are known as the reagents for the removal of primary and secondary amines from the mixture of primary, secondary, and tertiary amines.[2] These reagents react with primary and secondary amines, but not with tertiary amines.

Insoluble reagents containing functional groups introduced by chemical modification of polymer support will make the separation procedure simple and easy. Although a gel type cross-linked polystyrene (1.5% divinylbenzene) containing isothiocyanate group has been

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1) Location: *5-1, Oehonmachi, Kumamoto 862, Japan.*
2) R.L. Shriner, R.C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 5th ed., John Wiley and Sons, Inc., New York, 1966.

proposed as the insoluble Edman's reagent,3) this has not been extended to the separation of low molecular-weight amines. One of the major problems of the low cross-linked gel type resin is the lack of stability in organic solvents. This paper describes reactivity of a macroreticular (MR) resin containing isothiocyanate group (NCS resin) toward a variety of amines and an application for the removal of primary and secondary amines from sample solution.

Experimental

Chemicals and Apparatus——All the amines used in this experiment were commercial reagent grade, and used without purification.

NCS resin was prepared from MR type styrene-divinylbenzene (7.5% divinylbenzene) according to the method described previously.4) The probable structure of NCS resin is shown in Chart 1. *Anal.* Found: N, 5.65, S, 13.15. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2100 (NCS). The content of NCS group determined by the reaction with ethyl glycinate3) was 4.00 meq/g (value calculated from the N content, 4.03 meq/g).

Determination of the reactivity of NCS resin toward the amines was carried out by a gas chromatographic method by using a Shimadzu GC-4APF equipped with dual glass columns (1 m×4 mm I.D.) packed with 60—80 mesh Chromosorb 103. The column oven temperatures were 135—200°. The injection port and detector temperatures were maintained at 250°. For the analysis of contaminants in triethylamine, the columns (3 m) packed with 15% diglycerol and 5% tetraethylenepentamine5) on 30—60 mesh Shimalite were used.

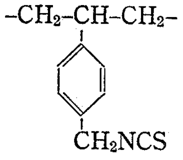

Chart 1

Combination gas chromatographic–mass spectrometric (GC–MS) analyses were performed on an JEOL-JMS 01SG instrument. The mass spectrometer was operated at an electron energy 27 eV.

Procedure——To a glass stoppered test tube (5 ml) containing NCS resin (50—100 mg), 1 ml of amine solution was added, then the mixture was shaken in a thermostat. After the shaking of a definite time, the mixture was cooled with running water to room temperature, and the amount of the amine remaining in the solution was determined by the gas chromatographic method.

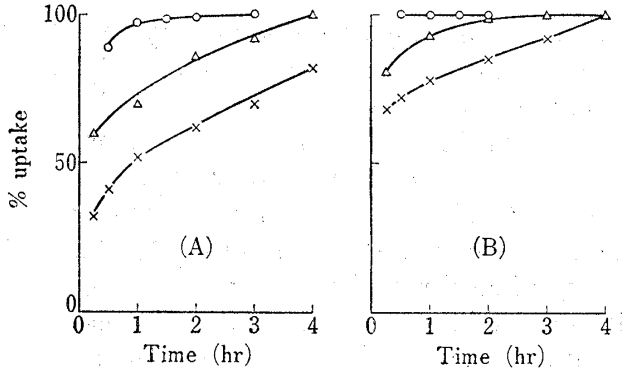

Fig. 1. Uptake of (A) Ethylamine and (B) Diethylamine at Varicus Temperatures

—○—: 50°, —△—: 35°, —×—: 20°.
One ml of amine aqueous solutions (0.05 M) was shaken with 50 mg of NCS resin.

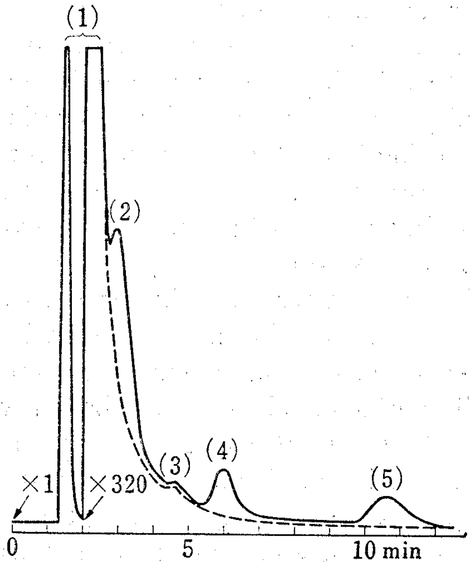

Fig. 2. Gas Chromatograms of Commercial Triethylamine

——: before shaking with NCS resin,
----: after shaking with NCS resin.
(1) triethylamine, (2) diethylamine, (3) unknown, (4) N-*n*-butylethylamine, (5) *n*-butylamine.
Column temperature: 60°.

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TABLE I. Percentage Uptake of Various Amines

Sample	Solvent	% uptake
Methylamine	Water	100
Ethylamine	Water	98.8
Ethylamine	Ethanol	99.6
n-Propylamine	Water	99.3
n-Butylamine	Water	100
n-Hexylamine	Water	100
Dimethylamine	Water	100
Diethylamine	Water	99.5
n-Dipropylamine	Water	100
N-*n*-Butylethylamine	Water	100
n-Dibutylamine	Ethanol	100
Isopropylamine	Water	97.3
Isopropylamine	Ethanol	98.7
Isobutylamine	Water	99.4
Isoamylamine	Water	99.4
sec-Butylamine	Water	99.1
tert-Butylamine	Water	54.4
tert-Butylamine	Ethanol	56.4
tert-Amylamine	Water	69.6
Aniline	Ethanol	54.5
N-Methylaniline	Ethanol	67.4
N-Ethylaniline	Ethanol	64.1

One ml of amine solutions (0.05 M) and 50 mg of NCS resin were shaken for 2 hr at 50°.

Results and Discussion

In a preliminary experiment, amine uptakes of NCS resin were examined at various temperatures by using aqueous solutions of ethylamine and diethylamine. As is shown in Fig. 1, the reaction rate of amine uptake increases with an increase in temperature. However, subsequent experiments were carried out at 50° because losses of amines having low boiling points due to volatility are not negligibly small at higher temperature. Diethylamine shows higher affinity than ethylamine for this resin.

Table I shows the percentage uptake of a variety of primary and secondary amines with NCS resin at 50°. The reactivities of the amines in ethanol solution are somewhat higher than those in aqueous solution. This is explained on the basis of swelling of NCS resin in ethanol solution. Most of the aliphatic amines showed higher affinity for this resin, except for primary amines having tertiary alkyl group, whereas aromatic amines showed lower affinity under the experimental condition. However, it was possible to raise the amine uptake with increasing of reaction time and amount of NCS resin; the uptake of aniline increased to 98% when 0.05 M aniline ethanol solution was shaken with 100 mg of NCS resin at 60° for 3 hr.

These data also suggest that the reactivities of NCS resin with the amines are not parallel to the basity of them. It is supposed that both of the basicity and steric effect of the substrates affect to the amine uptake of NCS resin.

This resin was applied to the purification of commercial triethylamine as an example of the application. As is shown in Fig. 2, the sample triethylamine contains four kinds of impurities which were identified by the GC–MS except for peak 3. When 1 ml of the sample and 100 mg of NCS resin were shaken for 4 hr at 50°, three impurities were retained on the resin. Trace amounts of impurities such as diethylamine, N-*n*-butylethylamine, and *n*-butylamine could be removed almost quantitatively from the triethylamine by using this resin.

This insoluble reagent has the advantage that it can be easily removed by filtration. In addition, this can be utilized in a variety of organic solvents because it is chemically and physically stable due to its MR structure.

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