The 1 : 1 Complex Formation of Triaryl Isocyanurates with Organic Solvents

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During the course of an investigation of isocyanate polymerization, it has been found that triaryl isocyanurates tend to form 1 : 1 complexes with various organic solvents.

TABLE I. ANALYTICAL DATA OF COMPLEXES
(R-NCO)$_3$-X

R	X	Composition	Analysis, %					
			Calcd.			Found		
			C	H	N	C	H	N
Phenyl	DMF	$C_{24}H_{22}N_4O_4$	66.96	5.15	13.02	66.99	5.17	12.95
p-Tolyl	DMF	$C_{27}H_{28}N_4O_4$	68.62	5.97	11.86	68.85	5.93	11.93
p-Tolyl	Benzene	$C_{30}H_{27}N_3O_3$	75.45	5.70	8.80	75.67	5.53	8.82
p-Tolyl	Acetone	$C_{27}H_{27}N_3O_4$	70.88	5.95	9.19	70.86	5.93	9.48
p-Methoxyphenyl	DMF	$C_{27}H_{28}N_4O_7$	62.30	5.42	10.76	61.55	5.20	10.70
p-Methoxyphenyl	Benzene	$C_{30}H_{27}N_3O_6$	68.56	5.18	8.00	68.55	5.30	7.90
p-Methoxyphenyl	Acetone	$C_{27}H_{27}N_3O_7$	64.15	5.38	8.71	64.04	5.34	8.60
p-Chlorophenyl	DMF	$C_{24}H_{19}N_4O_4Cl_3$	54.00	3.59	10.50	54.40	3.87	10.59
p-Chlorophenyl	Acetone	$C_{24}H_{18}N_3O_4Cl_3$*	55.56	3.50	8.10	55.37	3.53	7.94

* Cl: Calcd., 20.50%. Found, 20.67%.

TABLE II. C=O BAND FREQUENCIES OF 1 : 1 COMPLEXES (Nujol mull)

R	X	cm^{-1}
Phenyl	—	1710
Phenyl	DMF	1700, 1670
p-Tolyl	—	1765, 1715, 1690
p-Tolyl	DMF	1700, 1675
p-Tolyl	Benzene	1700
p-Tolyl	Acetone	1700
p-Methoxyphenyl	—	1765, 1715, 1690
p-Methoxyphenyl	DMF	1700, 1680
p-Methoxyphenyl	Benzene	1700
p-Methoxyphenyl	Acetone	1700
p-Chlorophenyl	—	1770, 1715, 1690
p-Chlorophenyl	DMF	1700, 1670
p-Chlorophenyl	Acetone	1700

Triaryl isocyanurates have previously been reported by Tsuzuki and his co-workers¹⁾ to form 1 : 1 complexes with alkylene carbonates, such as ethylene carbonate, propylene carbonate, and chloroethylene carbonate. This paper will discuss the formation of 1 : 1 complexes of triphenyl, tri-*p*-tolyl, tri-*p*-methoxyphenyl, and tri-*p*-chlorophenyl isocyanurates with *N, N*-dimethylformamide (DMF), benzene, and acetone.

When triaryl isocyanurates were boiled in such a solvent for about 2 hr., complexes were formed and isolated as colorless crystals on cooling or by the removal of the solvent. They were characterized by elemental analyses (Table I) and by infrared spectra analyses. The infrared absorption spectra of complexes contain almost all the principal bands of both components, but the relative intensity and the frequency of the C=O stretching absorption bands varied remarkably. The C=O bands of triaryl isocyanurates and complexes are summarized in Table II.

Methanol and ether did not form complexes with triaryl isocyanurates, and attempts to prepare such complexes as triphenyl isocyanurate-benzophenone and tri-*p*-tolyl isocyanurate-pyridine were unsuccessful.

The complex was stable for a long period at room temperature under reduced pressure, but it decomposed to the original two components on being heated above 100°C in vacuo. When the complexes of triphenyl isocyanurate-DMF and tri-*p*-methoxyphenyl isocyanurate-benzene were submitted to thermogravinometric analysis, there was observed a weight loss corresponding to the amount of the solvent in the complex in the temperature range from 70 to 150°C. The complexes show the melting points of the original triaryl isocyanurates because of the liberation of the solvents by the heating.

Experimental

Triaryl Isocyanurates.—Triphenyl isocyanurate (m. p. 280°C), tri-*p*-tolyl isocyanurate (m. p. 264°C), tri-*p*-methoxyphenyl isocyanurate (m. p. 260°C), and tri-*p*-chlorophenyl isocyanurate (m. p. 318°C) were prepared by the method given in the literature.²⁾

1 : 1 Complexes of Triaryl Isocyanurates with Solvents.—The data of the elemental analysis and the characteristic infrared absorption bands are listed in Table I and Table II respectively. They were prepared by the same procedure. A typical synthesis is described below.

The Synthesis of the Triphenyl Isocyanurate-DMF Complex.—Triphenyl isocyanurate (0.5 g.) was treated with boiling DMF (15 ml.) for 2 hr. After the reaction mixture had cooled, the DMF was removed by distillation under reduced pressure. The colorless crystals which were then precipitated were washed with ether. Yield, 83%.

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1) R. Tsuzuki, K. Ichikawa and M. Kase, *J. Org. Chem.*, **25**, 1009 (1960).

2) J. Idris Jones and N. G. Savill, *J. Chem. Soc.*, **1957**, 4392.