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Unsymmetrical Diisocyanates. II

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Synopsis

It has long been known that certain aromatic diisocyanates exhibit unequal reactivities of the two isocyanate groups. However, the degree of unsymmetry of reactivity in the previously known diisocyanates is limited. In this research, a number of structurally unsymmetrical diisocyanates were screened for unsymmetry of reactivity by reacting the diisocyanate with excess isoamyl alcohol in chlorobenzene solvent. The reaction was followed by observing the decrease of infrared absorption of the solution at 4.5 μ. A number of diisocyanates were found to have desirably high degrees of unsymmetry in reactivity. These diisocyanates, and the ratio of apparent half-lives of reaction for the two isocyanate groups are: 2,6-diethyl-*p*-phenylenediisocyanate, 100; 2,6-dimethyl-*p*-phenylenediisocyanate, 80; 2-bromo, 6-methyl-*p*-phenylenediisocyanate, 50; 2,6-dichloro-*p*-phenylenediisocyanate, 30; and 3,5-diethyl-4-4′-diisocyanato-diphenylmethane (DEMDI), 49.

Isocyanate groups in aromatic diisocyanates with unsymmetrically placed substituents react at different rates.[1,2] In particular, isocyanate groups in aromatic molecules containing a single *ortho* substituent react appreciably more slowly than unsubstituted aromatic isocyanates. In a previous paper, it was shown that the size of such an *ortho* substituent has relatively little effect on the ratio of the reaction rates of the two isocyanate groups.[3] However, it was found that the doubly hindered isocyanate group in 2,6-dichloro-*p*-phenylenediisocyanate is much less reactive than the unhindered group.

It was the purpose of the present study to synthesize a number of additional unsymmetrical diisocyanates and to determine their properties.

EXPERIMENTAL

Rate Measurements

The method of the previous paper[3] was employed without modification. Chlorobenzene was used as the solvent, and a 10-fold excess of isoamyl alcohol was used to react with the diisocyanate. The rate of disappearance of the isocyanate band at 4.5 μ in the infrared spectrum of the reaction mixture was measured with a Perkin-Elmer model 221 spectrophotometer. The infrared spectra were run in an air-conditioned room, which was maintained at about 21–23°C., but the reaction mixture itself in the ab-

sorption cell was not thermostatted. Many spectral determinations were made, and the smooth curve drawn through the data was used in determining the pseudo first-order rate constants after the reaction had proceeded to the extent of about 10–20% and after approximately 60–80% reaction had occurred. (The ratio of the apparent half-lives of reaction is only an approximate measure of the unsymmetry of a diisocyanate. For a more detailed discussion, see a recent paper on the topic.[4]) In this investigation some of the reaction rate constants were estimated to be accurate to two significant figures, and others to only one significant figure.

In all cases, the reaction mixture was 0.02*M* in isocyanate.

The reaction rates for the various diisocyanates are given in Table I. The second column lists the half-lives $\lambda_{1/2}$ computed from data at 10–20% reaction. In the third column are given $\lambda'_{1/2}$, the half lives of reaction after about 60–70% of the reaction had been completed. The last column lists the ratio of these half lives.

TABLE I
Relative Reactivities of Unsymmetrical Diisocyanates

Isocyanate	$\lambda_{1/2}$, min.	$\lambda'_{1/2}$, min.	$\lambda_{1/2}/\lambda_{1/2}$
2,6-Dimethyl-*p*-phenylene-diisocyanate	16	1.3×10^3	80
2,6-Diethyl-*p*-phenylenediisocyanate	24	2.4×10^3	1.0×10^2
2-Bromo-6-methyl-*p*-phenylenedi-isocyanate	8	3.9×10^2	50
2,6-Dichloro-*p*-phenylenediisocyanate	4	1.0×10^2	30
3,5-Diethyl-4,4′-diisocyanatodi-phenylmethane	33	1.6×10^3	49
2,4,6-Trimethyl-3,4′-diisocyanatodi-phenylmethane	62	6.8×10^2	11
3,5-Dimethyl-*X*,4′-diisocyanatodi-phenyl ether	61	4.4×10^2	7.2
2-Methyl-1,5-naphthylenediiso-cyanate	1.3×10^2	3.8×10^2	2.9
2,5-Dimethyl-4,4′-diisocyanatodi-phenylmethane	40	3.5×10^2	8.8

Preparation of Diamine Hydrochlorides

2,6-Dimethyl-*p*-phenylenediamine Dihydrochloride. This diamine was prepared according to the method of Noelting and Thesmar.[5] The diamine was dissolved in absolute ethanol and precipitated with concentrated aqueous HCl.

2,6-Diethyl-*p*-phenylenediamine Dihydrochloride. This diamine was prepared according to the above procedure and distilled at 172–177°C. at 11 mm. The diamine was then converted to the hydrochloride as above.

2-Bromo-6-methyl-*p*-phenylenediamine Dihydrochloride. This diamine was prepared by the bromination of 2-methyl-5-nitroaniline in acetic

acid.[6] The bromo compound in absolute ethanol solution was then reduced with Raney nickel and hydrogen at about 1500 psi and 100°C. The hydrochloride was recovered directly from the reaction mixture.

3,5-Diethyl-4,4′-diaminodiphenylmethane Dihydrochloride. A 149.4-g. portion of 2,6-diethylaniline was added to a mixture of 376 ml. of concentrated hydrochloric acid in 2000 ml. of water. After stirring, 140 ml. of formalin (37%) and 280.2 g. of aniline were added. The mixture was allowed to stand for 5½ hr., then heated to 72°C., and allowed to cool overnight. The precipitate was then filtered off. The solution was evaporated to a volume of 1 liter and cooled overnight. The crystals which precipitated were filtered off under suction, and weighed about 200 g. wet. The wet crystals were then recrystallized from 95% ethanol. The yield of 4,4′-diamino-3,5-diethyldiphenylmethane dihydrochloride was 108.0 g.

2,4,6-Trimethyl-3,4′-diiaminodiphenylmethane Dihydrochloride. To 50 ml. of mesitylene was added 11 g. of *p*-nitrobenzylchloride and about 0.5 g. anhydrous ferric chloride. The mixture was then heated, with stirring, to 40°C. Vigorous bubbling resulted. After standing for 30 min., the mixture was poured into water and the organic layer separated and again washed with water. The condensation product precipitated during the washing. The mother liquor was concentrated by evaporation, and another crop of crystals collected. After two recrystallizations from ethanol the product, 4-nitro-2′,4′, 6′-trimethyldiphenylmethane, melted at 117–117.5°C. The yield was 9.5 g.

The above compound, 7.6 g., was added slowly with stirring to 20 ml. red fuming nitric acid, the temperature being maintained below 40°C. with cooling. After standing for 5 min., the mixture was poured into water and washed. After two recrystallizations from glacial acetic acid, the product, 4,3′-dinitro-2′,4′,6′-trimethyldiphenylmethane, melted at 178–180°C.

The dinitro compound was reduced in ethanol solution with Raney nickel and hydrogen at about 1500 psi and 100°C. and recovered directly as the hydrochloride.

3,5-Dimethyl-*X*,4′-diaminodiphenylether Dihydrochloride. To 208 g. 3,5-dimethylphenol was added 80 g. of KOH, and the resulting mixture heated to solution.[7] Then, about 1 g. of active copper catalyst and 158 g. *p*-chloronitrobenzene were added, and the mixture refluxed for 5 hr. The mixture was cooled and allowed to crystallize. The mass was broken up and washed thoroughly with dilute NaOH solution, then with water. The product, 3,5-dimethyl-4′-nitrodiphenylether, was recrystallized from ethanol, and had a melting point of 76–77°C. The yield was 155 g., or 64%.

The nitroether, 40 g., was slowly added to 100 ml. fuming nitric acid, the temperature being kept below 40°C. After the mixture cooled, it was poured into water and washed. After recrystallization from acetone, the dinitro ether melted at 176–179°C., and the yield was 24 g., or 60%. A small amount of by-product also recovered, and had a melting point of 147–151°C. Because of the relationship of the melting points, it is pre-

sumed that the main product is the 4,4′-dinitro compound, and that the by-product is the 2,4′-dinitro compound.

In order to prove that neither product was 3,5-dimethyl-2′,4′-dinitrodiphenylether, this compound was synthesized. Potassium hydroxide, 16 g., was dissolved in 52 g. 3,5-dimethylphenol with heating, and 40 g. 2,4-dinitrochlorobenzene was added slowly with stirring. The mixture was allowed to cool and crystallize. After washing with KOH solution, followed by distilled water and subsequent recrystallization from ethanol, the product melted at 94–97°C.

The 3,5-dimethyl-4(?),4′-dinitrodiphenylether was reduced in ethanol solution with Raney nickel and hydrogen at about 1500 psi and 100°C. The diamine was recovered directly from the ethanol solution as the hydrochloride.

2-Methyl-1,5-naphthalenediamine Dihydrochloride. The 2-methyl-1,5-dinitronaphthalene was prepared according to the method of Vesely.[8] The dinitro compound was then reduced with hydrogen and Raney nickel and directly recovered as the hydrochloride.

2,5-Dimethyl-4,4′-diaminodiphenylmethane Dihydrochloride. About 1 g. anhydrous $FeCl_3$ was dissolved in 100 ml. *p*-xylene, and 16.9 g. *p*-nitrobenzylchloride was added. The mixture was then heated to 55°C. and cooled. After washing with water and drying over anhydrous calcium chloride, the mixture was distilled. The product, 2,5-dimethyl-4′-nitrodiphenylmethane boiled at 168–173°C. at about 2 mm. The product crystallized upon standing and was recrystallized from ethanol, m.p. 54–56°C.

To 15 ml. fuming nitric acid was added 6.8 g. of the mononitro compound, the temperature being kept below 60°C. The mixture was then added to water and washed. After three recrystallizations from acetic acid, the product, presumably 2,5-dimethyl-4,4′-dinitrodiphenylmethane, melted at 128–133°C.

The dinitro compound was reduced with Raney nickel and hydrogen and recovered as the hydrochloride from the ethanol solution.

2,3,4-Trimethyl-*X*,4′-diaminodiphenylmethane Dihydrochloride. To 50 ml. 1,2,3-trimethylbenzene was added about 0.5 g. anhydrous $FeCl_3$ and 11 g. *p*-nitrobenzylchloride. The mixture was heated to 85°C., a vigorous evolution of bubbles occurring. The mixture was then cooled, washed with water, and dried over calcium chloride. The mixture was then distilled, the product boiling at 199–207°C. at about 2 mm. Upon cooling, the product crystallized. Upon recrystallizing from ethanol the product, 2,3,4-trimethyl-4′-nitrodiphenylmethane, melted at 62–66°C.

To 14 ml. fuming nitric acid was added 6 g. of the mononitro compound, the temperature being kept below 33°C. A sandy precipitate formed as the reaction proceeded. After standing overnight, the reaction mixture was added to water and then washed. After two recrystallizations from glacial acetic acid, the product, 2,3,4-trimethyl-*X*,4′-dinitrodiphenylmethane, melted at 196–199°C.

The dinitro compound was reduced with Raney nickel and hydrogen, and the diamine crystallized from the reduction mixture, m.p. 168–170°C. The diamine was redissolved by heating, and recovered as a dihydrochloride.

***X*-Chloro-4′-methyl-*Y*,*Y*′-diaminodiphenyl Ether Dihydrochloride.** Potassium hydroxide, 20.2 g., was dissolved by heating in 51.3 g. solid *p*-cresol. After dissolution about 0.5 g. active copper powder catalyst was added, and 41.0 g. 3,4-dichloronitrobenzene was added in two portions. After the first addition, the temperature was 105°C. and an exothermic reaction started. After the second addition, the mixture was heated to 137°C. The product was washed many times with KOH solution, then water, and then distilled under vacuum. The boiling point was 185–187°C. at about 2 mm. The yield was 37 g. Since the product failed to crystallize, even on standing in the refrigerator, it is apparently a mixture of 2-chloro-4′-methyl-4-nitrodiphenyl ether, and 2-chloro-4′-methyl-5-nitrodiphenyl ether.

To 25 ml. fuming nitric acid was slowly added 12 g. of the above chloronitrocompound, the temperature being maintained below 20°C. The mixture was then added to water and washed. After three recrystallizations from ethanol, the product melted at 101–105°C., and presumably was the 2-chloro-4′-methyl-4,2′-dinitrodiphenyl ether. This product was combined with an additional crop of crystals and again recrystallized from ethanol. The melting point was now 86–98°C. Judging from the melting point data apparently at least two isomers were present. Since the isomers should have approximately the same reactivities, when converted to diisocyanates, the isomeric mixture was used in the preparation of the diisocyanate.

The isomeric mixture was reduced with hydrogen and Raney nickel and recovered as the dihydrochloride.

Preparation of Diisocyanates

All diisocyanates were prepared by phosgenation of the corresponding diamine hydrochlorides. Both *o*-dichlorobenzene and 1,2,4-trichlorobenzene were used as solvents. The preferred technique for phosgenation was the following. A 2-g. portion of diamine dihydrochloride was finely ground and then suspended in 250 ml. *o*-dichlorobenzene. Phosgene was then passed in, with stirring, for several hours until the solution was saturated. The solution was then slowly heated until all of the salt had dissolved, the flow of phosgene being maintained. The resulting clear solution was cooled to room temperature. The flow of phosgene was then stopped, and the excess phosgene was stripped out at 15–20 mm. pressure. The solution was concentrated to about 25 ml. under 15–20 mm. pressure, and then distilled at about 1 mm. pressure.

The properties of the isocyanates and derivatives are given below.

2,6-Dimethyl-*p*-phenylenediisocyanate. B. p. 155–160°C. at about 21 mm., m.p. 53–55°C. The dimethylurethane melts at 171–173°C.

2,6-Diethyl-*p*-phenylenediisocyanate. B. p. 167–170°C. at about 27 mm. The diethylurethane melts at 157–158°C.

2-Bromo-6-methyl-*p*-phenylenediisocyanate. B. p. 128–134°C. at about 1 mm., m.p. 46–53°C. The dimethylurethane melts at 187–189.5°C.

3,5-Diethyl-4,4′-diisocyanatodiphenylmethane. B. p. 222–230°C. at about 9 mm., and gradually crystallizes at room temperature. The dimethylurethane melts at 148–149°C.

2,4,6-Trimethyl-3,4′-diisocyanatodiphenylmethane. B. p. 235–252°C. at about 1 mm., m.p. 78–83°C. The dimethylurethane melts at about 160–164°C. with evolution of gas.

3,5-Dimethyl-*X*,4′-diisocyanatodiphenyl Ether. B. p. 217–226°C. at about 2 mm., m.p. 85–87°C. The dimethylurethane melts at 140–143°C.

2-Methyl-1,5-naphthylenediisocyanate. B. p. 165–170°C. at about 1 mm., m.p. 59–65°C. The dimethylurethane melts at 218–220°C.

2,5-Dimethyl-4,4′-diisocyanatodiphenylmethane. B. p. 223–230°C. at about 1 mm. The dimethylurethane melts at 209–214°C.

2,3,4-Trimethyl-*X*,4′-diisocyanatodiphenylmethane. The phosgenation proceeded properly, but the isocyanate could not be isolated from the mixture by vacuum distillation.

***X*-Chloro-4′-methyl-*Y*,*Y*′-diisocyanatodiphenyl Ether.** The phosgenation apparently proceeded properly, but the isocyanate could not be isolated.

DISCUSSION

Unsymmetrical diisocyanates with a large difference in reaction rates of the individual isocyanate groups have considerable utility in various special polyurethane formulations. If the two groups are of differing reactivity, the first group may be reacted while reserving the second group for a subsequent reaction, and if the two groups are of sufficiently different reactivity, it is possible to achieve almost complete selectivity in reaction.

The kinetic data in Table I demonstrate that the two isocyanate groups in the doubly hindered diisocyanates have a wide range of relative reactivities. The ratio of half lives varies from 7.2 to 100. The higher ratios are not surprising, since the isocyanate group flanked by two *ortho* substituents is not only highly hindered but also cannot be coplanar with the aromatic ring. Both effects should decrease the reactivity substantially, with respect to that of an unhindered isocyanate group on the same molecule. It is quite surprising, therefore, that such diisocyanates can exhibit reactivity ratios as low as 7.2 and 11. The fact that 3,5-dimethyl-*X*,4′-diisocyanatodiphenyl ether has a reactivity ratio of 6.2 suggests that this compound is actually 3,5-dimethyl-2,4′-diisocyanatodiphenyl ether. From a molecular model, it is seen that the *o*-phenyl ether group actually exhibits relatively little steric effect on the isocyanate group. In the case of the supposed 2,4,6-trimethyl-3,4′-diisocyanatodiphenylmethane no such explanation is available. The only reasonable possibilities are (*1*) the compound

actually exhibits anomalous reactivities, and (2) the mesitylene was isomerized during the reaction with ferric chloride, so that the supposed structure is incorrect.

The other singly hindered diisocyanates studied in this investigation were selected as likely candidates for high reactivity ratios. In each case, not only was one isocyanate group hindered by the presence of one *ortho* substituents, but the same group was also deactivated by a number of electron-donating substituents on the aromatic ring. These diisocyanates showed reactivity ratios intermediate between those of the simple singly hindered diisocyanates and those of the doubly hindered diisocyanates, as expected.

These very unsymmetrical diisocyanates should be useful in special polyurethane elastomers in which it is desired to achieve maximum efficiency of use of the diisocyanate and maximum control over the various stages of chemical reaction. These diisocyanates should also be useful in one-package polyurethane varnish and adhesive formulations in which maximum shelflife as well as efficiency and control is desired. Preliminary experiments with DEMDI (3,5-diethyl-4,4′-diisocyanatodiphenylmethane) in one-package varnish formulations have demonstrated the predicted advantages. A formulation with DEMDI substituted for TDI on an equimolar basis shows greatly increased shelf life. Alternatively, much less DEMDI (roughly one-half the number of mols) may be used without decreasing shelf life. Finally, DEMDI may be used in a catalyzed formulation to give very rapid drying times without causing shortened shelf life.

References

1. Bailey, M. E., V. Kirss, and R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).
2. Pelley, R. L., U. S. Pat. 2,757,184, July 31, 1956.
3. Case, L. C., *J. Chem. Eng. Data*, **5**, 347 (1960).
4. Case, L. C., *J. Polymer Sci.*, **48**, 27 (1960).
5. Noelting, E., and G. Thesmar, *Ber.*, **35**, 628 (1902).
6. Gibson, C. S., and J. D. A. Johnson, *J. Chem. Soc.*, **1929**, 1245.
7. Brewster, R. Q., and T. Groening, *Org. Syntheses*, **2**, 445 (1943).
8. Vesely, V., and J. Kapp, *Rec. Trav. Chim.*, **44**, 360 (1925).

Résumé

Il est connu depuis longtemps que certains diisocyanates aromatiques présentent des réactivités inégales des deux groupes isocyanates. Cependant la différence de réactivité des diisocyanates actuellement connus est limitée. Dans cette recherche un nombre de diisocyanates structurellement asymétriques ont été protégés quant à l'asymétrie de réactivité en faisant réagir le diisocyanate avec un excès d'alcool isoamylique dans le chlorobenzène comme solvant. La réaction a été suivie en observant la diminution d'absorption infra-rouge de la solution à 4.5 microns. Un certain nombre de diisocyanates ont été trouvés posséder un haut degré souhaitable d'asymétrie dans la réactivité. Ces diisocyanates et le rapport des temps de demi-décomposition en cours de réaction pour les deux groupes isocyanates sont: diisocyanate de *p*-phénylène-2,6-diéthyl, 100; diisocyanate de 2,6-diméthyl-*p*-phénylène, 80; diisocyanate de 2-bromo-6-méthyl-*p*-phénylène, 50; diisocyanate de 2,6-dichloro-*p*-phénylène, 30; et 3,5-diéthyl-4,4-diisocyanate-diphénylméthane (DEMDI), 49.

Zusammenfassung

Es ist schon lange bekannt, dass gewisse aromatische Diisocyanate eine ungleiche Reaktionsfähigkeit der beiden Isocyanatgruppen zeigen. Der Grad der Unsymmetrie der Reaktionsfähigkeit bei den bis jetzt bekannten Diisocyanaten ist aber begrenzt. In der vorliegenden Untersuchung wurden eine Anzahl von Diisocyanaten mit unsymmetrischer Struktur auf die Unsymmetrie ihrer Reaktionsfähigkeit durch Reaktion der Diisocyanate mit überschüssigem Amylalkohol in Chlorbenzol als Lösungsmittel untersucht. Die Reaktion wurde durch Beobachtung der Abnahme der Infrarotabsorption der Lösung bei 4,5 Mikron verfolgt. Eine Reihe von Diisocyanaten zeigten den erwünschten grossen Unsymmetriegrad der Reaktionsfähigkeit. Bei diesen Isocyanaten wurden folgende Verhältnisse der scheinbaren Halbwertszeit der Reaktion der beiden Isocyanatgruppen gefunden: 2,6-Diäthyl-*p*-phenylendiisocyanat, 100; 2,6-Dimethyl-*p*-phenylenediisocyanat, 80; 2-Brom-6-methyl-*p*-phenylenediisocyanat, 50; 2,6-Dichlor-*p*-phenylendiisocyanat, 30; 3 5-Diäthyl-4,4′-diisocyanatodiphenylmethan (DEMDI), 49.

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