Dimerisation and Trimerisation of 2,4 Tolylene Di-isocyanate

By A. DAVIS

(Eingegangen am 20. Mai 1963)

SUMMARY:

2,4 tolylene di-isocyanate can form a dimer (TDID) and a trimer (TDIT). For bulk polymerisation at temperatures in the range 40 °C. to 100 °C. the initial rates of these processes are given by the expressions,

$$\frac{d[TDID]}{dt} = 6.6 \cdot 10^3 \text{ e } \frac{-21,000}{\text{RT}} \text{ moles} \cdot \text{cc}^{-1} \cdot \text{sec}^{-1} \text{ and}$$
$$\frac{d[TDIT]}{dt} = 0.175 \text{ e } \frac{-16,000}{\text{RT}} \text{ moles} \cdot \text{cc}^{-1} \cdot \text{sec}^{-1}$$

At each temperature the rate of trimerisation remained essentially constant over the conversion range examined, but the rate of dimerisation decreased gradually to zero. The equilibrium concentrations of TDID at 78 °C. and 100 °C. were 8.5 per cent and 7.1 per cent respectively.

Experimental evidence indicated that under the conditions examined (i) only oligomers resulting from interaction between isocyanate groups in the 4-position were important in dimerisation and trimerisation, and (ii) the trimerisation process was independent of the dimerisation process.

Assuming the kinetics of dimerisation to be represented by

$$2\text{TDI} \stackrel{\mathbf{k}_{1}}{\rightleftharpoons} \text{TDID}$$

$$\mathbf{k}_{2}$$
values for \mathbf{k}_{1} (1.5 · 10⁸ e $\frac{-21,000}{\text{RT}}$ moles · cc⁻¹ · sec⁻¹) and

$$\mathbf{k}_{2}(5.1 \cdot 10^{9} \text{ e} \frac{-23,300}{\text{RT}} \text{ sec}^{-1}) \text{ were obtained.}$$

This investigation shows that the dimerisation and trimerisation of 2,4-TDI are not important competing processes in the cure of a polyurethane. However as appreciable amounts of TDID and TDIT can be formed as a result of prolonged storage at elevated temperatures it is important that the purity of the isocyanate is determined immediately before use.

196

ZUSAMMENFASSUNG:

2,4-Toluoldiisocyanat kann ein Dimeres (TDID) und ein Trimeres (TDIT) bilden. Bei der Polymerisation in Substanz im Temperaturbereich von 40 bis 100°C gilt für die Anfangsgeschwindigkeiten

$$\frac{\mathrm{d[TDID]}}{\mathrm{dt}} = 6.6 \cdot 10^{-3} \cdot \mathrm{e} \frac{-21\,000}{\mathrm{RT}} \,\mathrm{Mole} \cdot \mathrm{ccm}^{-1} \cdot \mathrm{sec}^{-1} \,\mathrm{und}$$
$$\frac{\mathrm{d}[\mathrm{TDIT]}}{\mathrm{dt}} = 0.175 \cdot \mathrm{e} \,\frac{-16\,000}{\mathrm{RT}} \,\mathrm{Mole} \cdot \mathrm{ccm}^{-1} \cdot \mathrm{sec}^{-1}$$

Bei jeder Temperatur blieb die Trimerisierungsgeschwindigkeit im untersuchten Umsetzungsbereich im großen und ganzen konstant, während die Dimerisierungsgeschwindigkeit allmählich auf Null absank. Die Gleichgewichtskonzentrationen von TDID bei 78 und 100°C waren 8,5 bzw. 7,1%. Unter den Versuchsbedingungen kamen 1. nur die sich von der Isocyanatgruppe in 4-Stellung ergebenden Oligomere bei der Di- und Trimerisation in Betracht, und 2. war die Trimerisierungs- von der Dimerisierungsreaktion unabhängig. Nimmt man für die Kinetik der Dimerisation den Vorgang

$$\begin{array}{c} \mathbf{K_1} \\ \mathbf{2} \operatorname{TDI} \rightleftharpoons \\ \mathbf{K_2} \\ \end{array} \operatorname{TDIP}$$

an, so erhält man für

$$K_1 = 1,5 \cdot 10^8 \cdot e \frac{-21\,000}{RT} \text{ Mole} \cdot \text{ccm}^{-1} \cdot \text{sec}^{-1} \text{ und } K_2 = 5,1 \cdot 10^9 \cdot e \frac{-23\,300}{RT} \cdot \text{sec}^{-1}$$

Nach den Ergebnissen spielt die Di- und Trimerisierung von 2,4-TDI bei der Herstellung der Polyurethane keine große Rolle. Indessen können sich bei langer Lagerung und erhöhter Temperatur merkbare Mengen an TDID und TDIT bilden, so daß es wichtig ist, die Reinheit des Isocyanats unmittelbar vor Gebrauch zu bestimmen.

Introduction

Polyurethane elastomers can be formed by the reaction of hydroxyterminated polyesters or polyethers with a di-isocyanate, usually tolylene 2,4-di-isocyanate (TDI) or a mixture of the 2,4 and 2,6 isomers. A small degree of trifunctionality is introduced to give a weakly cross-linked, extensible rubber by including a triol in the reacting system. The principal reaction is thus that of a hydroxyl with an isocyanate group to form a urethane linkage. Side reactions producing allophanates, amides, ureas and biurets may occur¹) but are undesirable. While all these groups have intermolecular forces (*i.e.* cohesive energy densities) comparable to or greater than that of the urethane group none of them is as flexible²): in addition reactions forming allophanates and biurets produce cross-linking. The net result is to increase the rigidity of the elastomer. Other reactions which may occur during the cure of a polyurethane elastomer are the formation of tolylene 2,4 di-isocyanate dimer (TDID) and trimer (TDIT),



The formation of appreciable amounts of these oligomers of TDI could have a marked effect upon the physical properties of the resulting elastomers. The number of free isocyanate groups available for the desired urethane reaction would be reduced and it has been shown that the final physical properties of the elastomer are very dependent on the hydroxyl to isocyanate ratio³). In addition the uretedione ring of TDID can be partially opened to give a trifunctional entity⁴) which like the trifunctional trimer would act as an additional cross-linking agent during cure. The cross-links so formed from TDID and TDIT would also be less flexible than those formed from the normal cross-linking agent (aliphatic polyols) because of the rigidity of the benzene ring structure.

The ability of aryl isocyanates to form dimers and trimers under certain conditions has been known for more than 80 years⁵). A variety of methods, which essentially involve treating the monomer with traces of a basic catalyst (e.g. pyridine, triethylamine, triethyl phosphine), have been developed to form these materials⁶). The result is that many dimers and trimers have been isolated and characterised⁷).

There is no information in the literature about the rates of dimerisation and trimerisation of TDI.

Experimental

Materials

2,4 and 2,6 TDI were redistilled under vacuum ($126-127^{\circ}C$. and $129-130^{\circ}C$./18 Torr respectively) before use.

The dimer of 2,4 TDI, prepared by the method given by RAIFORD and FREYERMUTH⁶), had a melting point of 154°C. The molecular weight, 343, determined by measuring the depression of the freezing point of nitrobenzene was in good agreement with the theoretical value of 348. A volumetric estimation of the purity of the TDID (explained below) gave 102 per cent.

A trimer of TDI was formed but could not be isolated because of its high solubility in TDI. Attempts to isolate this trimer by vacuum distillation of the excess TDI resulted in the formation of a viscous material which was believed to be a polymer of the TDIT.

Estimation by Titration of Tolylene 2,4 Di-isocyanate Dimer plus Trimer in a Mixture Containing Monomer

TREMBLAY and BOIVIN⁸) developed a method for estimating the dimer of TDI in the presence of the monomer. They found that under certain conditions a weak base dicyclohexylamine will only react with the free isocyanate groups of TDID and leave untouched the uretedione ring. As it is reasonable to assume that the more stable 6-membered ring of the trimer would also be unaffected by dicyclohexylamine, the method of TREMBLAY and BOIVIN was developed to estimate dimer plus trimer.

The procedure was to reflux about 0.5 g. TDI/TDID/TDIT mixture with 50 ml. of approximately 0.2 N dicyclohexylamine (redistilled, $145-146^{\circ}C./30$ Torr) for three minutes. The solution was then diluted with 50 ml. of isopropyl alcohol and the excess amine titrated with standard HCl (about 0.1 N) in isopropyl alcohol. The end-point was determined with a mixed indicator of bromphenol blue and methyl red. A blank estimation omitting the TDI/TDID/TDIT mixture was made.

The per cent TDID + TDIT (by wt.) is given by the expression

% (TDID + TDIT) =
$$200 - \frac{17.4 \cdot (\text{Blank} - \text{Titre}) \cdot N}{\text{wt. of (TDI + TDID + TDIT)}}$$

where N is the normality of the HCl.

Determination of Tolylene 2,4 Di-isocyanate Dimer by Infrared Analysis

It was found by comparing the infrared spectra of TDI and TDID that the latter had a characteristic peak at 5.6 μ . A straight line calibration of OD_{5.6} μ against [TDID] was obtained when various amounts of TDID were dissolved in CCl₄. Using a cell, 0.42 mm. thick the calibration curve could be expressed in the form,

g.TDID/100 g.
$$CCl_4 = 0.31 \cdot (OD_{5,6} \mu)$$
.

Determination of Tolylene 2,4 Di-isocyanate Trimer

It would appear that TDIT is formed from TDI in the presence and absence of ferric acetyl acetonate a catalyst often used in the cure of a polyurethane elastomer. Infrared spectra of both systems reveal an absorption peak or peaks in the range $5.75-5.85 \mu$ which is the wavelength region of carbonyl absorption peaks characteristic of other substituted phenyl isocyanate trimers⁷ and of trimeric polymers of TDI⁹. By combining the volumetric estimation of TDID plus TDIT with the infrared analysis for TDID it was possible to calibrate [TDIT] (in CCl₄) against OD_{5.8} μ . Using a 0.42 mm. cell a straight line plot was obtained which could be expressed in the form,

g. TDIT/100 g.
$$CCl_4 = 0.50 \cdot (OD_{5.8} \mu)$$

A. DAVIS

Results

In initial experiments the rates of dimerisation and trimerisation of pure 2,4 TDI were determined at a variety of temperatures (Fig. 1 and 2). It was found that the maximum rate of dimerisation occurred initially, thereafter the rate decreased gradually to zero at a particular equilibrium



Fig. 1. The rate of dimerisation of 2,4 TDI at various temperatures (equilibrium concentration after approximately 1500 hrs. at 78° C. = 8.5%)

Fig. 2. The rate of trimerisation of 2,4 TDI at various temperatures

concentration of TDID. The initial rate of dimerisation was increased by increasing the temperature, the initial dimerisation process having an activation energy of 21 kcal./mole (Fig. 3). Another effect of increasing the temperature was to decrease the equilibrium concentration of TDID. The equilibrium concentration of TDID at 78° and 100°C. were 8.5 percent and 7.1 percent respectively.

The rate of trimerisation of pure 2,4 TDI remained essentially constant throughout the range of conversion examined (Fig. 2). A variation of temperature gave an activation energy of about 16 kcal./mole for the initial trimerisation process (Fig. 3).



Fig. 3. The effect of temperature on the initial rate of dimerisation and trimerisation of 2,4 TDI. \triangle – dimerisation; \odot – trimerisation

From Fig. 1 and 2 it would appear that the rate of trimerisation was independent of [TDID]. This was verified by adding 8 percent TDID to pure TDI when it was found that the rate of trimerisation was the same as that of pure TDI.

To obtain some idea of the contribution made to the overall rate of dimerisation and trimerisation of 2,4 TDI by 2,2 dimerisation and 2,2,2 trimerisation, the rates of dimerisation and trimerisation of 2,6 TDI at 100 °C. were examined. These were found to be 1 percent and 5 percent respectively of the corresponding rates for 2,4 TDI.

Discussion

As 2,4 tolylene di-isocyanate is an unsymmetrical molecule it may form three isomeric dimers and four isomeric trimers. However from steric considerations the dimer and trimer formed from interaction between isocyanate groups in the 4 position should be favoured. There is evidence that this is so. Molecular weight and isocyanate determinations on the solid precipitated from 2,4 TDI indicate it to be a dimer. This dimer is probably unique and not a mixture of 4,4 2,2 and 2,4 dimers because it has a sharp melting point. It cannot be the 2,2 dimer because 2,6 TDI does not dimerise readily. Also the 2,4 dimer cannot be formed in appreciable amounts as this one would probably result in a polymer. It would appear, therefore, that the dimer formed must be the 4,4 isomer.

The fact that the rate of trimerisation is independent of the rate of dimerisation suggests that quite separate mechanisms are involved. If the kinetics of dimerisation can be represented by the equation,

$$\begin{array}{c} k_1 \\ 2 \text{ TDI} \rightleftharpoons \text{ TDID} \\ k_2 \end{array} \tag{1}$$

then initially, when [TDID] = 0,

$$\frac{d[TDID]}{dt} = k_1 \cdot [TDI]^2$$
(2)

and at equilibrium,

$$\mathbf{k}_1 \cdot [\text{TDI}]^2 = \mathbf{k}_2 \cdot [\text{TDID}] \tag{3}$$

From the experimental results it can be shown that the initial rate of dimerisation is represented by the expression,

$$\frac{d[TDID]}{dt} = 6.6 \cdot 10^3 e \frac{-21,000}{RT} \text{ moles} \cdot cc^{-1} \cdot sec^{-1}$$
(4)

and, therefore, from (2) and (4)

$$k_1 = 1.5 \cdot 10^8 e \frac{-21,000}{RT} cc \cdot moles^{-1} \cdot sec^{-1}$$
 (5)

From the equilibrium concentrations of TDI and TDID at 78 °C. and 100 °C. the difference between activation energies of the forward and reverse reactions (E_1-E_2) was calculated to be -2.3 kcal./mole. Knowing, therefore, that $E_2 = 23.3$ kcal./mole and using (3) and (5) it can be deduced that,

$$k_2 = 5.1 \cdot 10^9 e \frac{-23,300}{RT} sec^{-1}$$
 (6)

The collision frequencies for 1st and 2nd order reactions are of the order of $10^{13}-10^{14} \sec^{-1}$ and $10^{14}-10^{15} \csc \cdot moles^{-1} \cdot \sec^{-1}$ respectively. The preexponential values obtained for the forward and reverse reactions, assuming (1) as representing the mechanism, require therefore that the p factors for the formation and decomposition of TDID are of the order of 10^{-7} and 10^{-4} respectively. These values are low but not unknown¹⁰. Considering the resonance hybrid structures of an isocyanate

$$\begin{array}{ccc} R - \stackrel{\Theta}{\overline{N}} - \stackrel{\Theta}{\overline{C}} = \overline{0}| \ \rightleftharpoons \ R - N = C = 0 \ \rightleftharpoons \ R - N = C - \stackrel{\Theta}{\overline{0}} \stackrel{\Theta}{\overline{0}} \\ I & II \end{array}$$

molecular orbital theory predicts that structure II is more representative of an isocyanate than structure I. It seems probable that dimerisation involves structure I and this could explain the low p factors found. The low p factors could be an indication, however, that the overall dimerisation process is not represented by the simple relationship 2 TDI \rightleftharpoons TDID. These points might be clarified by further experimental work aimed at determining the rate laws which govern the dimerisation process, as well as by examining the effect of varying the electro-negativity of R on the rate of dimerisation.

From the experimental results the initial rate of trimerisation in the uncatalysed system is given by the expression:

$$\frac{d[TDIT]}{dt} = 0.175 \text{ e } \frac{-16,000}{RT} \text{ moles} \cdot \text{cc}^{-1} \cdot \text{sec}^{-1}$$
(7)

Assuming the simple mechanism

$$3 \text{ TDI} \rightarrow \text{TDIT}$$
 (8)

the above expression becomes

$$\frac{d[TDIT]}{dt} = 6 \cdot 10^5 \ [TDI]^3 \ e \ \frac{-16,000}{RT} \ moles \cdot cc^{-1} \cdot sec^{-1}$$
(9)

The pre-exponential factor is far below the collision frequency of third order reactions $(10^{15}-10^{16} \text{ cc.}^2 \cdot \text{moles}^{-2} \cdot \text{sec}^{-1})$ and it seems likely that the kinetics of trimerisation are more complicated than suggested in (8).

Importance of Dimerisation and Trimerisation in Cure of Polyurethane

In the cure of a polyester or polyether polyurethane at 60 °C. a common cure temperature, the more active para isocyanate groups of 2,4 TDI should be consumed in urethane formation inside 10 minutes even with no catalyst present¹¹). This investigation shows therefore that the dimerisation and trimerisation of TDI are not important competing processes in a cure of a polyurethane as only insignificant amounts of TDID and TDIT can be formed in 10 minutes at 60 °C. However appreciable amounts of TDID and TDIT can be formed as a result of prolonged storage of the TDI at elevated temperatures. It is important therefore that the purity of the isocyanate is determined, preferably by infrared methods immediately before use.

Thanks are due to Mr. D. J. HENSHAW for assistance with some of the volumetric estimations.

- ¹⁾ H. L. HEISS, F. P. COMBS, P. J. GEMEINHARDT, J. H. SAUNDERS, and E. E. HARDY, Ind. Engng. Chem. 51 (1959) 929.
- ²⁾ J. H. SAUNDERS, Rubber Chem. Technol. 33 (1960) 1259.
- ³⁾ T. L. SMITH and A. B. MAGNUSSON, J. Polymer Sci. 42 (1960) 391.
- 4) J. H. SAUNDERS and E. E. HARDY, J. Amer. chem. Soc. 75 (1953) 5439.
- ⁵⁾ V. MIGRDICHIAN, The Chemistry of Organic Cyanogen Compounds, Reinhold, New York 1947, p. 349.
- ⁶⁾ J. I. JONES and N. G. SAVILL, J. chem. Soc. [London] 1957, 4392.
- ⁷⁾ R. G. ARNOLD, J. A. NELSON, and J. J. VERBANC, Chem. Reviews 57 (1957) 47.
- ⁸⁾ M. TREMBLAY and J. L. BOIVIN, unpublished Canadian Armament Research and Development Establishment report.
- ⁹⁾ Brit. P. 809,809 (1959); H. FRANCE and A. LISTER.
- ¹⁰ A. A. FROST and R. G. PEARSON, Kinetics and Mechanisms, Wiley and Sons, New York, 1953, p. 100.
- ¹¹⁾ M. A. DEISZ and M. OHTA, University of Akron, Institute of Rubber Research, Final Report March 1955-March 1957.