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THE THERMAL DISSOCIATION OF PHENOL-BLOCKED TOLUENE DIISOCYANATE CROSSLINKERS

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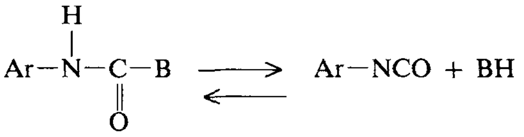
ABSTRACT

The thermal dissociation reaction of different phenol-blocked toluene diisocyanate crosslinkers has been studied by the use of differential scanning calorimetry. It was found that dissociation occurs after melting of the adduct. The dissociation reaction rate constants, activation energies, and the heat of reaction values are reported. Adducts with ortho-substituted phenols dissociate at a faster rate than those with para isomers. The regeneration of isocyanate functionality was identified by an infrared spectrophotometer.

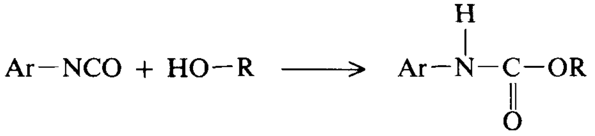
INTRODUCTION

Most polyurethanes are manufactured with polyols containing a terminal secondary hydroxyl group [1]. The reactivity of the secondary hydroxyl group with isocyanate is relatively lower than that of the primary hydroxyl group [2, 3]. Some polyols [e.g., poly(oxypropylene)-poly(oxyethylene) copolymers, poly(oxytetramethylene) glycols and hydroxyl-terminated polybutadienes with primary hydroxyl groups] are used in the polyurethane industry. In some applications (e.g., single package blocked adduct urethane coatings, solid propellants, etc.) they suffer from a lower pot life due to their higher reactivity with isocyanates. The use of blocked diisocyanates instead of diisocyanates as crosslinkers improves pot life and extends the scope of application.

The concept of blocked isocyanates is illustrated by



$$\mathrm{Ar{-}\overset{\overset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}B \rightleftarrows Ar{-}NCO + BH} \qquad (1)$$



$$\mathrm{Ar{-}NCO + HO{-}R \longrightarrow Ar{-}\overset{\overset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}OR} \qquad (2)$$

where BH is the blocking agent which is a thermally removable active hydrogen compound. Phenol is a classical example. The blocked isocyanate is stable in the presence of alcohols and water at ambient temperature, but dissociates to regenerate the isocyanate functionality at elevated temperatures and can react with hydroxy compounds to form urethane linkages which are thermally more stable. Carlson and coworkers [4] studied the cure mechanism of blocked isocyanate with hydroxy functional acrylic resin. They found that in the initial stages the dissociation reaction occurs much faster than the subsequent cure reaction between regenerated isocyanate and the hydroxy compound.

There has been no systematic investigation on the dissociation reaction of phenol-blocked diisocyanate crosslinkers. For the use of such crosslinkers in practical applications, it is necessary to determine the heat of reaction values and the kinetic parameters. In this report we describe the dissociation reaction of a number of substituted phenol-blocked toluene diisocyanates by employing infrared spectra for the analysis of regenerated isocyanate functionality.

EXPERIMENTAL

Materials

Preparative methods for phenol-blocked toluene diisocyanate (TDI) adducts were reported in our previous publication [5]. All the samples were repeatedly reprecipitated in toluene and used for differential scanning calorimetric (DSC) and IR spectral studies.

Analytical Methods

Nonisothermal DSC studies were conducted using the Mettler TA 3000 system. The samples were sealed in aluminum pans and the scans were made from 35 to 500°C at a heating rate of 10°C/min under nitrogen purge. The IR spectra for each adduct were recorded twice in a Perkin-Elmer Model 781 spectrophotometer. In the first experiment, 0.05 g of the adduct was dissolved in 10 mL chloroform at room temperature. The IR cell was filled with this solution, and the spectrum was scanned over the 4000–400 cm^{-1} range. In the second experiment, 0.05 g of the adduct was taken in a boiling tube and heated for 5 minutes at 170°C. Then the adduct was cooled and dissolved in 10 mL chloroform. The spectrum was scanned immediately over the 2500–1500 cm^{-1} range. For both experiments an IR cell with a 0.2-mm cavity thickness was used.

Data Analysis Method

Willard's [6] methodology was adopted to determine the kinetic parameters from the DSC curves. For the first-order kinetics, the reaction rate constant was calculated by

$$\frac{dH(tT)/dt}{\Delta H_0 - H(tT)} = k$$

where $dH(tT)/dt$ = heat flow into the sample (J/g·s), $H(tT)$ = partial heat of reaction (J/g), and ΔH_0 = total heat of reaction (J/g). In this method the DSC curves were digitized manually for the 190 to 240°C temperature range by 10°C increments. The numerator in the rate equation was calculated by measuring the height of the ordinate at selected temperatures and converting it to J/s. The determination of $\Delta H_0 - H(tT)$ represents the area to the right of the ordinate and was converted to J/g. As shown in the rate equation, the rate constants k were calculated directly from the ratio of $dH(tT)/dt$ to $\Delta H_0 - H(tT)$.

RESULTS AND DISCUSSION

In a blocked isocyanate the bond between the carbonyl carbon and the oxygen of the urethane linkage (—NHCOO—) is labile. Since this bond is broken in the deblocking reaction when heat is applied, there should be an endothermic transition. DSC techniques are ideal for the quantitative measurement of the heat of the dissociation reaction as well as for the determination of the kinetic parameters.

All adducts except that of 2,6-dimethylphenol show two endothermic transitions in the DSC curves (Fig. 1). The first transition, which is very sharp, corresponds to the melting of the compounds. The reported melting points of these adducts [5] coincide with the peak temperatures (T_m) of the first transition of the corresponding adduct (Table 1). The sharpness of this peak indicates that the compounds are pure [7]. The second endotherm starts immediately after the completion of the first endothermic transition. This pattern confirms that the dissociation reaction starts after the melting of the adducts. Conversely, TDI blocked with 2,6-dimethylphenol shows only one endothermic transition. The endotherm due to the melting of the adduct is absent. It may be concluded that melting with dissociation occurs in the case of the 2,6-dimethylphenol–TDI adduct.

The first-order rate constants were calculated over temperatures ranging from 190 to 230°C. A linear regression analysis was performed on the data to give the best fit of the Arrhenius plot (Fig. 2). Since the linearity of the data is good, it can be concluded that the assumption on the reaction order is correct. The calculated rate constants and the apparent activation energies are given in Table 2. As predicted [5, 8], the electron-releasing substituent reduces the dissociation reaction rate and the electron-withdrawing substituent increases the rate. For example, TDI blocked with *m*-cresol, *p*-cresol, and 2,6-dimethylphenol dissociates at a lower rate, and TDI blocked with chlorophenols dissociates at a higher rate than the phenol-

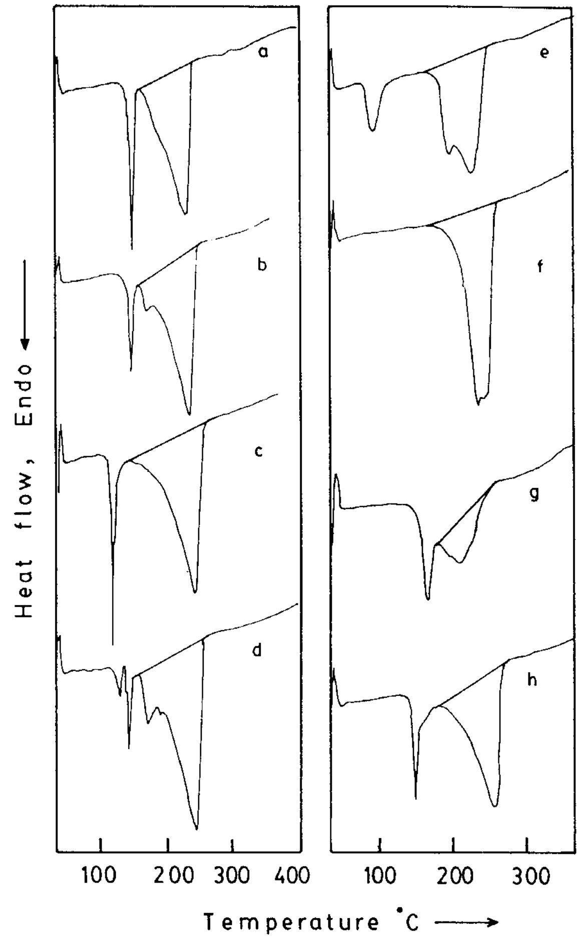


FIG. 1. DSC curves of the adducts of TDI with (a) phenol, (b) *o*-cresol, (c) *m*-cresol, (d) *p*-cresol, (e) *o*-methoxyphenol, (f) 2,6-dimethylphenol, (g) *o*-chlorophenol, and (h) *p*-chlorophenol.

TABLE 1. Melting Endotherms of Phenol-Blocked TDI Adducts

Adduct	T_m, °C	mp, °C [5]
Phenol-TDI	150	145-150
o-Cresol-TDI	152	150-155
m-Cresol-TDI	120	118-120
p-Cresol-TDI	145	145-150
o-Methoxyphenol-TDI	95	95-100
2,6-Dimethylphenol-TDI	—	155-160
o-Chlorophenol-TDI	155	150-155
p-Chlorophenol-TDI	138	133-136
2,4-Di-*t*-butylphenol-TDI	156	155-160

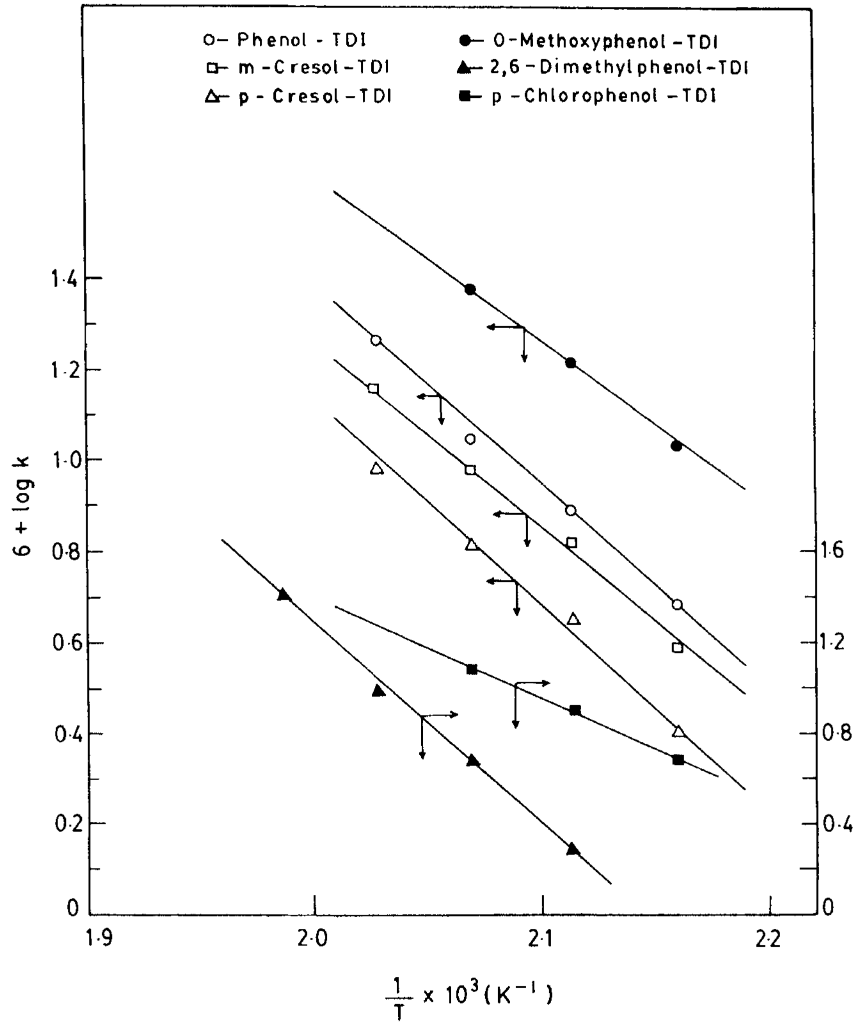


FIG. 2. Arrhenius plots for dissociation reaction of phenol-blocked TDI adducts.

TABLE 2. Kinetic Parameters and Heat of Reaction Values for the Thermal Dissociation of Phenol-Blocked TDI Adducts

	First-order rate constants, $k \times 10^6 \text{ s}^{-1}$					E_a,	ΔH_0,
Adduct	190°C	200°C	210°C	220°C	230°C	kJ·mol^{-1}	J·g^{-1}
Phenol-TDI	4.8	7.6	10.8	18.3	37.8	83	379
o-Cresol-TDI	5.0	7.7	10.8	17.0	32.1	76	428
m-Cresol-TDI	3.9	6.9	9.7	14.6	28.7	81	459
p-Cresol-TDI	2.5	4.5	6.3	9.2	14.4	87	737
o-Methoxyphenol-TDI	10.5	16.4	23.5	39.4	72.4	75	264
2,6-Dimethylphenol-TDI	–	1.9	4.8	9.6	25.5	168	306
o-Chlorophenol-TDI	11.2	16.6	27.0	60.9	–	81	120
p-Chlorophenol-TDI	4.8	8.0	11.4	20.9	36.7	81	229
2,4-Di-*t*-butylphenol-TDI	6.0	10.2	15.3	29.5	81.8	84	149

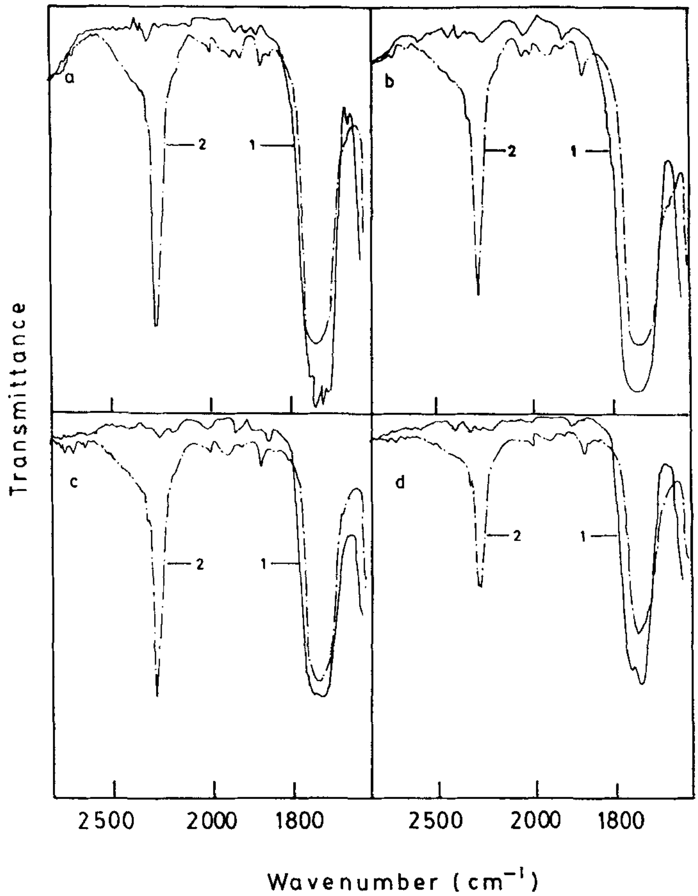


FIG. 3. IR spectra for before (1) and after (2) heating the adducts of TDI with (a) phenol, (b) *o*-methoxyphenol, (c) 2,6-dimethylphenol, and (d) *p*-chlorophenol.

blocked TDI adduct. Adducts with ortho substituents in the phenolic moiety dissociate at a higher rate than adducts with para substituents. This may be attributed to the steric effect. Mukaiyama and Iwanami [9] reported that the ortho substituents accelerate the dissociation regardless of their nature and facilitate the deprotonation of the urethane linkage. The effect of steric hindrance on deprotonation of the urethane linkage is highly pronounced in the dissociation reaction of the *o*-methoxyphenol–TDI adduct. This adduct has the lowest activation energy and twice the rate constant of the *o*-cresol–TDI adduct. In contrast with the methyl group in the ortho position, the 2,6-dimethylphenol–TDI adduct shows a low rate constant and the highest activation energy. It can be concluded that the electronic effect predominates over the steric effect.

The activation energies (E_a) decreases with increasing rate constants. The E_a value (19.8 kcal/83 kJ) for the dissociation reaction of the phenol–TDI adduct is comparable with the reported value (21.4 kcal) for the dissociation reaction of *N*-phenyl-benzylcarbamate [9]. Carlson and coworkers [4] reported a somewhat higher activation energy (33.4 kcal) for the deblocking reaction of the phenol-blocked trimerized isophorone diisocyanate adduct.

DSC measures the heat flow into (endothermic) or out (exothermic) of a sample over a specified temperature range. This heat of reaction (ΔH_0) is specific for a particular compound. In this study, nine compounds with different structures were used, and the corresponding heat of reaction values are given in Table 2. They also confirm the effect of substituents on the deblocking reaction.

The IR spectra taken before and after heating the adducts are given in Fig. 3. All spectra obtained before heating the adducts do not show any absorption band in the 2250–2270 cm^{-1} range. If any free isocyanate group is present in the adduct, it will strongly absorb in this region. The absence of a peak indicates that the isocyanate functionality is completely suppressed by the blocking agents. However, the spectra obtained after heating above the melting temperatures of the adducts show a strong absorption band in the 2250–2270 cm^{-1} range due to the regenerated isocyanate functionality. At the same time, the intensity of the urethane carbonyl group at 1700 cm^{-1} is reduced. This is due to cleavage of the labile bond in the urethane linkages at elevated temperatures.

CONCLUSIONS

This report is the first to describe the thermal dissociation reaction of a number of phenol-blocked TDI crosslinkers. The reported rate constants (k), activation energy (E_a), and the heat of reaction values (ΔH_0) will be used to design better blocked diisocyanate crosslinkers for industrial applications.

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