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Thermal Stability of Isocyanate-Based Polymers. 1. Kinetics of the Thermal Dissociation of Urethane, Oxazolidone, and Isocyanurate Groups

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ABSTRACT: The kinetics of thermal dissociation of urethane, oxazolidone, and isocyanurate groups were measured on model compounds [5-(phenoxymethyl)-3-phenyl-2-oxazolidinone (I), 5-(phenoxymethyl)-3-cyclohexyl-2-oxazolidinone (II), 1,3,5-triphenyl-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (III), 1,3,5-tricyclohexyl-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (IV), and butyl phenylcarbamate] by using and IR-sealed ampule method, developed for these measurements. The kinetics of the initial stage of the thermal decomposition of the model compounds followed first-order kinetics and the kinetic parameters E_a, A, and T_D were determined. It was found that thermal stability of the above-mentioned groups increased in the following order: carbamate < oxazolidone < isocyanurate. The activation energies increased in the same order. Model oxazolidones with the cycloaliphatic substituent on the nitrogen had higher thermal stability than oxazolidones with the aromatic (phenyl) substituent. The cleavage of the oxazolidone rings proceeded through the formation of carbon dioxide and other intermediates which further decomposed, forming aniline, phenol, and various hydrocarbons.

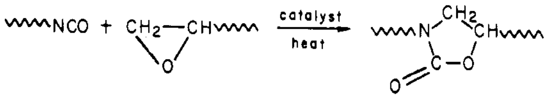
Introduction

Urethane block copolymers have found in recent years a variety of applications in industry as cellular materials, elastomers, coatings, and sealants. In general, these polymers have excellent mechanical properties; however, their use is limited by the relatively low thermostability of the urethane group present in their chain. The thermal stability of urethanes depends on the type of isocyanates and polyols used in their preparation and has a relatively wide temperature range. In general, the presence of electron-donating substituents on the nitrogen and oxygen of the urethane group increases thermal stability and the presence of electron-withdrawing groups decreases the thermal stability of urethane linkages in polymer chains.[1]

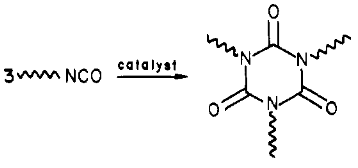
The thermal stability of urethane block copolymers increases in the following structural order:[2] aryl-NHCOO-aryl < alkyl-NHCOO-aryl < aryl-NHCOO-alkyl < alkyl-NHCOO-alkyl.

The need to increase the thermal stability of these block copolymers has led to the introduction of more heat-resistant heterocyclic groups into the polymer chain.[3] Such heterocyclic groups, which can be prepared from isocyanates, are oxazolidones and isocyanurates.

The oxazolidone rings can be synthesized via the cycloaddition of isocyanate groups to epoxide groups according to the following scheme:[4-8]



The isocyanurate rings can be formed via cyclotrimerization of isocyanates:[9]



The resulting isocyanurate rings form thermostable cross-links in the polymer network.

At the present time very few kinetic data exist in the literature regarding the thermal stability of urethane, oxazolidone, and isocyanurate groups.[10-15] Usually these kinetic data were obtained by means of thermogravimetric analysis (TGA) or from the analysis of decomposition products. The accuracy of these kinetic measurements is affected by the variable volatility of degradation products and is complicated by possible parallel and/or consecutive decomposition reactions. These open-system methods are not suitable for monitoring the thermal decomposition of model compounds which very often are volatile.

In this paper the thermal stability of oxazolidone, isocyanurate, and urethane groups was determined by measuring the kinetics of the initial stage of the thermal cleavage of each individual group using model compounds and IR spectrophotometry.

Experimental Section

Preparation of Model Compounds. All the reactions for the preparation of model compounds were carried out in an apparatus that had been dried at 150 °C for 3 h. The apparatus was assembled under nitrogen which was previously passed through traps containing sulfuric acid, sodium hydroxide, and a 5-ft column containing glass beads and phosphorus pentoxide. The isocyanates used were previously purified by distillation. Spectrograde solvents were further purified by distillation over the appropriate drying agent.

5-(Phenoxymethyl)-3-phenyl-2-oxazolidinone (I). Phenyl isocyanate (0.2 mol) and 3-phenoxy-1,2-propylene oxide (0.2 mol) were heated in 100 mL of 2-ethoxyethyl acetate with 0.5 mmol of diethylzinc as catalyst. The reaction mixture was stirred at 150 °C for 10 h and then poured into 600 mL of diethyl ether and kept at 0 °C for 12 h. The precipitate was filtered and washed several times with diethyl ether to yield 19.9 g (70.6% yield) of product. Purification was carried out by repeated recrystallizations from benzene and diethyl ether. The product had a melting point of 135 °C; IR 1760 cm^{-1} (ν(C=O)).

Anal. Calcd for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6. Found: C, 71.5; H, 5.6.

5-(Phenoxymethyl)-3-cyclohexyl-2-oxazolidinone (II). Cyclohexyl isocyanate (0.2 mol) and 3-phenoxy-1,2-propylene oxide (0.2 mol) were heated in 100 mL of 2-ethoxyethyl acetate with 0.5 mmol of diethylzinc as catalyst. The reaction mixture was stirred at 150 °C for 10 h to yield 14 g (50.9% yield) of product. Purification was carried out in the same manner as in the case of I. The product had a melting point of 137-138 °C; IR 1740 cm^{-1} (ν(C=O)).

Anal. Calcd for $C_{16}H_{21}O_3N$: C, 69.8; H, 7.7. Found: C, 69.9; H, 7.9.

1,3,5-Triphenyl-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (III). Phenyl isocyanate (0.92 mol) was mixed with 100 mL of pure acetone in the presence of 0.5% (w/w based on isocyanate) trimerization catalyst (mixture of 20% solution of potassium acetate in ethylene glycol with 2,4,6-tris[(dimethylamino)-

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methyl]phenol (DMP-30), [DMP-30]/[solution] = 4/1). The mixture was stirred for 5 h at 70 °C and then poured into 600 mL of benzene. The precipitate was purified by repeated recrystallizations from acetone and benzene. The product had a melting point of 281 °C (lit.[27] mp 281); IR 1710 cm^{-1} (ν(C=O)).

Anal. Calcd for $C_{21}H_{15}O_3N_3$: C, 70.6; H, 4.2. Found: C, 71.1; H, 4.5.

1,3,5-Tricyclohexyl-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (IV). Cyclohexyl isocyanate (0.23 mol) and 50 mL of dimethylformamide were mixed in the presence of 1% (w/w based on isocyanate) sodium ethoxide. The mixture was stirred for 24 h at 70 °C. Subsequently it was cooled to -50 °C. The precipitate was filtered and recrystallized from DMF. The cyclohexyl isocyanurate (IV) thus obtained had a melting point of 140 °C; IR 1690 cm^{-1} (ν(C=O)).

Anal. Calcd for $C_{21}H_{33}O_3N_3$: C, 67.2; H, 8.8. Found: C, 67.3; H, 8.9.

Butyl Phenylcarbamate (V). Butyl phenylcarbamate was prepared according to the method described by David and Staley.[27]

The product after recrystallization from diethyl ether had a melting point of 62 °C; IR 1735 cm^{-1} (ν(C=O)).

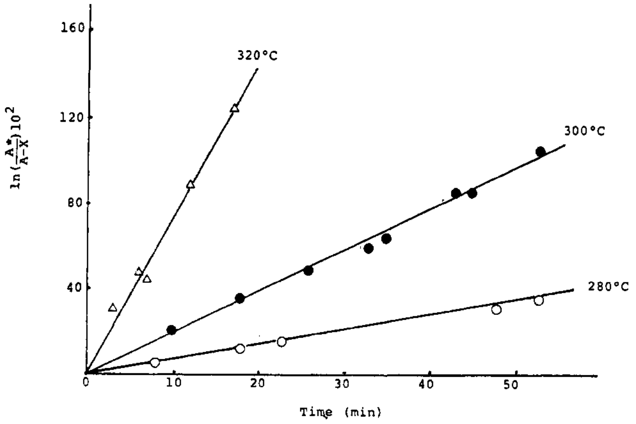
Degradation Studies. Kinetic Measurements. The kinetics of decomposition of the above-mentioned model compounds were measured by using the following technique: into ampules (dimensions L = 18 cm, o.d. = 1 cm, i.d. = 0.5 cm; 10/30 ground joint at the open end) were placed small amounts (0.05–0.1 g) of model compounds. The ampules were connected to a vacuum line and a vacuum of 10^{-3} mmHg was applied for 30 min. Atmospheric pressure was restored by passing N_2 into the vacuum line. This procedure was repeated five times. The ampules were then sealed under vacuum, covered with a metal screen, and placed into a high-temperature bath in a vertical position (bath composition: 40% $NaNO_2$, 7% $NaNO_3$, 50% KNO_3). Variations in temperature were kept below 2 °C. The ampules were taken out of the bath at selected time intervals. They were then cooled down in less than 1 min to room temperature by means of an air stream followed by immersion in water. In the case of butyl phenylcarbamate, the ampules were quenched with liquid nitrogen in order to prevent recombination of the degradation products (alcohol and isocyanate). The rates of thermal degradation of the model compounds were determined from the rate of disappearance of IR peaks characteristic for each compound. The calibration curves showed that the quantitative relationship between transmittance and concentration was consistent with the Beer–Lambert law.

Analytical Methods. HPLC analyses were carried out on a 30 cm × 4 mm i.d. μ-Bondapack C_{18} column (chloroform solvent) with a Model 202 HPLC chromatograph (Waters Associates) equipped with a VK-6 sample loop, a Model 6000A solvent delivery system, UV and RI detectors (Waters Associates), and a recorder (Houston Instruments).

Gas chromatographic analyses were carried out with a Hewlett-Packard HP5840A gas chromatograph equipped with thermal conductivity and flame ionization detectors.

Results and Discussion

The kinetics of the initial stage of the thermal degradation of carbamate, oxazolidone, and isocyanurate groups were studied on model compounds I–IV using IR spectrophotometry as an analytical tool. It was observed that during degradation of the above-mentioned models, the absorption peaks assigned to the stretching C=O vibrations of carbamate (ν_{CO} 1735 cm^{-1}), oxazolidone (ν_{CO} 1740 or 1760 cm^{-1}), and isocyanurate groups (ν_{CO} 1710 cm^{-1}) decreased and in fully decomposed compounds were completely absent. The degradation products did not interfere and therefore this method was utilized for the quantitative determination of the conversion of the thermal degradation of the model compounds. In order to eliminate possible experimental errors due to the volatility of the model compounds, all degradation kinetic studies were carried out in closed systems using the ampule technique. The kinetics of degradation was measured under isothermal conditions.



*A = 100

Figure 1. Kinetics of thermal decomposition of butyl phenylcarbamate (V).

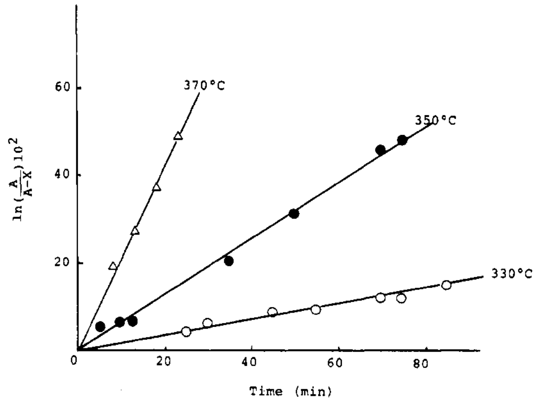


Figure 2. Kinetics of thermal decomposition of 5-(phenoxymethyl)-3-phenyl-2-oxazolidinone (I).

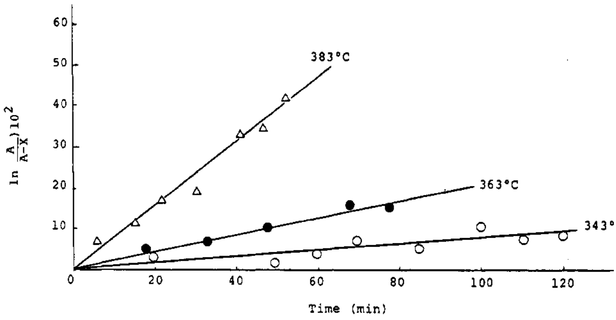


Figure 3. Kinetics of thermal decomposition of 5-(phenoxymethyl)-3-cyclohexyl-2-oxazolidinone (II).

It was determined that the kinetics of thermal degradation of I–IV were first order with respect to the concentration of carbamate, oxazolidone, or isocyanurate groups present in the system

$$dx/dt = k(a - x) \tag{1}$$

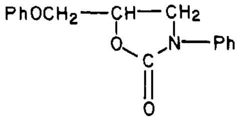
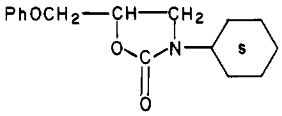
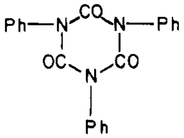
where a is the initial concentration and $(a - x)$ is the concentration of undecomposed groups in the system at time t.

The values of the rate constants of degradation, k, were determined by using the integrated form of eq 1:

$$\ln [a/(a - x)] = kt \tag{2}$$

The integrated forms of the first-order time plots for the model compounds are presented in Figures 1–4. The values of the rate constants were determined by least squares and the results are summarized in Table I. The thermal degradations were studied at three different tem-

Table I
Kinetic Parameters of the Thermal Decomposition of Model Compounds

model compound	structure	T, °C	10^3k, min^{-1}	E_a, kJ mol^{-1}	A, min^{-1}	T_D, °C, at k = 0.005 min^{-1}
I		330 350 370	1.629 5.649 19.2	201.1	4.30×10^{14}	348
II		343 363 383	0.617 2.028 7.565	209.6	3.54×10^{14}	376
III		400 420 440	1.683 5.638 20.906	252.2	6.15×10^{16}	417
V	PhNHCOOBu	280 300 320	6.447 19.816 69.567	161.8	1.23×10^{13}	277

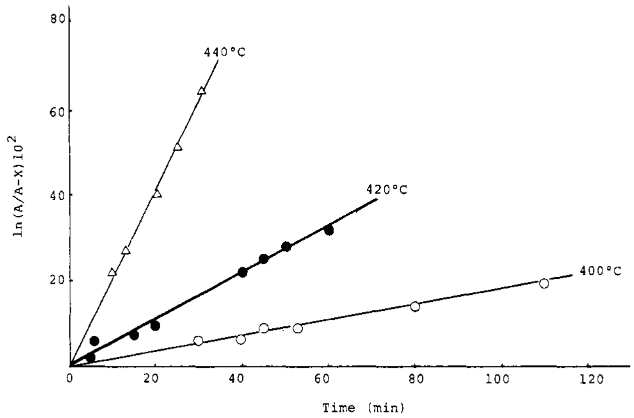
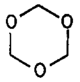
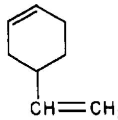
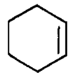


Figure 4. Kinetics of thermal decomposition of 1,3,5-triphenyl-*s*-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (III).

Table II
Kinetic Parameters of the Thermal Decomposition of Cyclic Compounds

model compound	E_a, kJ mol^{-1}	A, min^{-1}	ref
 $\longrightarrow 3CH_2O$	198.4	6.0×10^{16}	17
 $\longrightarrow$ 2Btd	259.5	9.5×10^{16}	20
 $\longrightarrow C_2H_4$ + Btd	277.1	9.5×10^{16}	18
 $\longrightarrow 2C_2H_4$	261.6	2.3×10^{17}	19
 $\longrightarrow C_2H_4 + CH_2O$	251.1	3.0×10^{16}	22

peratures in order to obtain activation energies and frequency factors. The activation energy, E_a, and the frequency factor, A, were calculated from the Arrhenius equation (Table I).

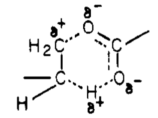
The values of activation energies for the cleavage of oxazolidone, isocyanurate, and carbamate groups were compared with values reported in the literature.

Bald et al.[12] reported an activation energy of 130.6 kJ for the thermal decomposition of the oxazolidone ring. This value is relatively low in comparison with the value obtained in this study and values reported in the literature for other cyclic compounds which range from 196.7 to 276.2 kJ (Table II).

In the case of urethanes, Dyer et al. reported activation energies of decomposition in the range 129.7–146.5 kJ.[10,11] These values are in relatively good agreement with our data and other literature data.[16]

The frequency factor (A = 6.15×10^{16} min^{-1}) for the decomposition of the isocyanurate ring is in good agreement with values reported for the decomposition of trioxane (A = 6×10^{16} min^{-1}) and other similar cyclic compounds (Table II).

This order of the frequency factor is typical for decompositions through six-center cyclic transition states, which proceed with very small changes in activation entropy.[21] The lower value of the frequency factor (A = 4.3×10^{14} min^{-1}) for decomposition of the oxazolidones is probably associated with a decrease of activation entropy, due to the formation of a tighter (distorted) transition complex. A distorted transition complex was suggested[21] for the decomposition of cyclobutene and cyclohexene, where lower values of the frequency factor were also determined. The low value of the frequency factor for the decomposition of the urethane group (A = 1.23×10^{13} min^{-1}) is probably associated with the formation of a six-membered cyclic transition complex. Similar transition complexes were postulated in the case of thermal decomposition of ester groups:[22]



The formation of this complex results in a decrease in activation entropy, due to the loss of free rotation around the C–O bond of the urethane group.

In order to compare quantitatively the thermal stability of carbamate, oxazolidone, and isocyanurate groups, the decomposition temperature (T_D) at which model compounds decomposed at the same rate was calculated. The rate constant k = 0.005 min^{-1} was chosen arbitrarily and represents a 25.9% decomposition of model compound at

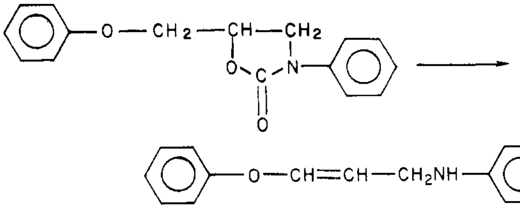
Table III
Products of the Thermal Decomposition of 5-(Phenoxymethyl)-3-phenyl-2-oxazolidinone (I)[c]

product	method	retention time, min
PhOH	HPLC	3.45
$PhNH_2$	HPLC	3.17
H_2	GC	1.22
CH_4	GC	3.60
CO	GC	4.51
CO_2	GC	7.08
C_2H_4	GC	8.47
C_2H_6	GC	9.41
$C_3H_6 + C_3H_8$	GC	13.91
C_4 fraction	GC	19.39

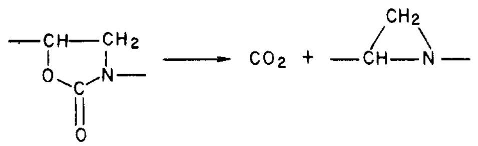
the thermal exposure of 1 h. Results of calculated T_D values are shown in Table I. As can be seen from this table, the oxazolidone model compound I decomposes at the same rate as the carbamate V but at a 71 °C higher temperature. Similarly, the difference in T_D between isocyanurate III and oxazolidone I is 69 °C.

It has been reported in the literature[24] that polyurethanes prepared from aliphatic isocyanates exhibit a higher thermal stability than those prepared from aromatic isocyanates. A similar phenomenon was observed in our studies of model oxazolidones. Results presented in Table I show that oxazolidone II, with a cycloaliphatic substituent on the N atom, exhibited a higher thermal stability than oxazolidone I, with an aromatic substituent. However, in the case of model isocyanurate compound IV, prepared from cyclohexyl isocyanate, the thermal stability was found to be lower than that of model isocyanurate III, prepared from phenyl isocyanate. It was determined by analysis of degradation products that the cyclohexyl group decomposed at 380 °C and subsequently destabilized the isocyanurate ring. Similar results were also reported by Sullivan[25] and Pasek,[26] who investigated decomposition at various cyclohexyl compounds and found similar decomposition temperatures.

The decomposition of model oxazolidone I was carried out at 340 °C for 3 h and the products were analyzed by GC and HPLC techniques. The results are shown in Table III. From these data and from data reported by Bald et al.[12] and Braun et al.[23], decomposition proceeds through cleavage of oxazolidone ring and evolution of CO_2. This cleavage, according to Bald, leads to the formation of the following intermediate:



On the other hand, Braun believes that the cleavage leads to azirine-type intermediates:



The formation of three-membered rings was verified by mass spectroscopic measurements of the decomposition of oxazolidones.[23] However, from our data it seems that these intermediates form, through further decomposition, aniline, phenol, and various hydrocarbon types of products.

Conclusions

The kinetics of thermal dissociation of carbamate, oxazolidone, and isocyanurate groups were measured on model compounds by using IR techniques. The kinetics of the initial stage of the thermal decomposition of the model compounds followed first-order kinetics. It was found that the thermal stability of the above-mentioned groups increased in the following order: carbamate < oxazolidone < isocyanurate. The substituents on the rings had a strong effect on the thermal stability of model compounds. The presence of electron-donating substituents on nitrogen increased the thermal stability and the presence of electron-withdrawing groups decreased the thermal stability of oxazolidone rings.

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