

The Chemistry of Blocked Isocyanates. I. Kinetics and Mechanism of the Reaction of Macromolecular Benzophenone Oxime Carbamates with Dibutylamine

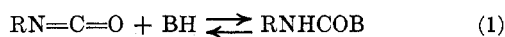
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Dibutylamine reacts with benzophenone oxime carbamates to give the corresponding dibutylureas. This reaction, with a polymeric bis(oxime carbamate) derived from a toluene-2,4-diisocyanate-polypropylene oxide adduct, was studied in toluene solution using kinetic techniques. The reaction exhibited first-order kinetics and had entropy of activation of -1.86 eu and enthalpy of activation of 24.8 kcal/mol, and the rate was insensitive to added tertiary amine. The reaction was favored by electron-releasing substituents on the oxime moiety with $\rho = -0.45$. An intramolecular, cyclic transition state is postulated for the rate-determining dissociation step.

Blocked polyurethanes are those polymers whose reactive isocyanate groups have been treated (eq 1)



with a thermally removable active hydrogen compound, BH. The term "unblocking" may refer to dissociation of the unstable adduct or to the reaction of a blocked polyurethane with some monomeric or polymeric co-reactant. In this paper, unblocking will be used to indicate the latter (eq 2), whereas the reverse reaction in eq 1 will be referred to as dissociation.



The thermal dissociation and unblocking of isocyanate adducts have been studied by several workers. Interchange of the ester portion of a carbamate with an alcohol higher boiling than that from which the carbamate was derived is well known. Ben-Ishai and Katchalski¹ and Gaylord and Sroog² further extended the scope of this reaction, the latter authors using lower boiling alcohols and acid catalysis. The mechanism of this transesterification may involve dissociation as a first step. There is some evidence³ which implies such an equilibrium, although much of the data of Gaylord and Sroog² as well as more recent evidence⁴ are not adequately explained by this hypothesis, and a duality of mechanism has been proposed.²

The thermal dissociation of urethanes and ureas in the presence of coreactants was the subject of extensive investigations of Mukaiyama and collaborators.^{5,6} They have established that isocyanates are intermediates in the reactions of urethanes under a variety of conditions. A general base catalyzed double-proton transfer was proposed on the basis of kinetics data. Additional studies of thermal reactions of monomeric and polymeric urethanes in the presence of coreactants or catalysts have been made by several workers and have been reviewed.⁷

Dyer and coworkers^{8,9} have studied the thermal degradation of carbamates in the absence of coreactants. Dissociation *via* a cyclic intramolecular transition state appears to be the first step in a series of reactions which provides numerous products.

Investigations more closely related to the use of blocked polyurethanes have centered around determination of minimum unblocking temperatures.^{7,10} At least one coreactant was present in all such studies.

There have apparently been no kinetic experiments related to unblocking in which the blocking agent was an oxime, although at least one commercial product is based on such a structure. We undertook to study the unblocking of oxime carbamates in the hope that a low-temperature unblocking polyurethane coating system could be developed. This paper reports the results of investigation of the kinetics of unblocking of aromatic ketoximes based on benzophenone from an isocyanate terminated polyether.

Experimental Section

Melting points are uncorrected. Infrared spectra (ir) were determined on a Perkin-Elmer Model 457 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were run on a Joelco Minimar at ambient temperature in deuteriochloroform solution. Tetramethylsilane was used as internal standard. Benzophenone, substituted ketones, hydroxylamine hydrochloride, and toluene-2,4-diisocyanate (TDI) were used as purchased from Eastman Organic Chemicals. Solvents were reagent or electronic grade and were dried over activated 4A molecular sieve. Poly(propylene oxide) was supplied by Wyandotte Chemicals Corp. (Pluracol 1040).

Synthesis of Oximes.—A stirred solution of ketone, hydroxylamine hydrochloride, and pyridine (1 equiv each) in anhydrous ethanol was heated to reflux and the temperature was held for 2 hr. The cooled solutions were concentrated under reduced pressure and the product was precipitated by adding it to faintly alkaline (NH_3) water, collected on a Büchner funnel, washed, and dried. The oximes were recrystallized from methanol to constant melting behavior. In the case of oximes of substituted benzophenones, two distinct melting ranges were observed, corresponding to the syn and anti isomers. Table I lists the properties of the oximes including the approximate syn:anti ratio determined by nmr.

Preparation of Blocked Urethane Prepolymers (Polymers 1-4).—Poly(propylene oxide) of average mol wt 1040 was added dropwise and with stirring to a toluene solution of TDI so as to give a prepolymer solution with nonvolatiles' content of 75%. A dry nitrogen atmosphere was maintained and ice-water cooling was used to keep the temperature below 50° . After addition, the reaction mixture was held until the isocyanate content was

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 (3) T. L. Davis and K. C. Blanchard, *J. Amer. Chem. Soc.*, **51**, 1801 (1929).
 (4) N. G. Gaylord, *J. Org. Chem.*, **25**, 1874 (1960).
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 (6) T. Mukaiyama and Y. Hoshino, *ibid.*, **78**, 1946 (1956), and references therein.
 (7) For reviews of polyurethane chemistry, see (a) S. G. Entelis and O. V. Nestrov, *Russ. Chem. Rev.*, **35**, 917 (1966); (b) J. H. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology," Vol. I, Interscience, N. Y., 1962; (c) A. Damusis and K. C. Frisch in "Treatise on Coatings," R. R. Myers and J. S. Long, Eds., Vol. I, Part I, Dekkar, New York, N. Y., 1967, Chapter 12.

(8) E. Dyer and G. E. Newborn, Jr., *J. Amer. Chem. Soc.*, **80**, 5495 (1958).
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 (10) H. E. Hill, C. S. Pietras, and D. J. Damico, *J. Paint Technol.*, **43**, 55 (1971).

TABLE I

SYNTHESIS OF BENZOPHENONE OXIMES BY THE PYRIDINE METHOD

Para substituent	% yield, pure	Isomer	Mp, °C		Estimated syn:anti ^a (by nmr)
			Found ^a	Lit. ^b	
H	95		143.5-144.5	144	
OCH ₃	79	Syn	116-120	115-116	50:50
		Anti	137-142	137-138	
Cl	36	Syn	94	95	5:95
		Anti	156-159	155-156	
NO ₂	51	Syn	115-116	115	40:60
		Anti	136-143	158	

^a Syn and anti with reference to the substituted aromatic ring; two distinct melting ranges were observed. ^b Values were taken from Beilstein.

constant, as determined by the dibutylamine procedure.¹¹ When a constant per cent NCO, equal to that predicted for reaction of one-half of the TDI originally present, was obtained, the solution was diluted with toluene and the calculated amount of solid oxime was added. The mixture was held at 50° until a solution was obtained and no isocyanate could be detected. The final solution had a nonvolatiles' content of 75%.

A check on the extent of blocking was made by heating a sample of blocked polymer containing a known excess of dibutylamine, added as a standardized toluene solution, under reflux for 15 min. After cooling and dilution with 2-propanol, the remaining amine was titrated with HCl to a bromocresol green end point and the equivalent weight of the blocked polymer solution was determined. The polymers prepared are shown in Figure 1.

Preparation of the Bis(dibutylurea) of TDI-Terminated Poly(propylene oxide) (Polymer 5).—To a solution of isocyanate-terminated polyether prepared as discussed above was added an amount of dibutylamine equal to the concentration of free NCO. The resulting solution was stirred until no NCO could be detected by the dibutylamine procedure.¹¹

Kinetic Measurements.—Solutions of dibutylamine in 100 ml of toluene and blocked prepolymer in 250 ml of the same solvent were simultaneously equilibrated in a Lab-Line constant-temperature water bath. Temperature was controlled to $\pm 0.05^\circ$ using a mercury-contact thermoregulator. A slick of mineral oil was floated over the bath water to limit evaporation and increase precision of the control. An ASTM standardized thermometer was used to measure temperature.

After a 30-min equilibration period, the polymer solution was diluted with the amine solution with vigorous mixing and a timer was started. Initial reactant concentrations ranged from 0.0242 to 0.242 N.

At measured time intervals 10-ml aliquots of reaction mixture were withdrawn and quenched in 100 ml of 2-propanol. The quenched solutions were titrated with 0.1 N aqueous HCl to the yellow bromocresol green end point. The volume of HCl used in the titration (in milliliters) was thus equal to 100 times the molar concentration of dibutylamine in the reaction mixture at the time of sampling.

First-order rate constants were taken as the least-squares slopes of plots of $\ln([\text{dibutylamine}]_{\text{time } t} - [\text{dibutylamine}]_{\text{time } \infty})$ vs. time. The infinity value of concentration was measured after the expiration of 10 half-lives. Least-squares analysis was performed by computer. Half-lives were also obtained from hand-drawn first-order plots. Attempts to fit the data to higher order kinetic plots did not provide straight lines. The minimum acceptable correlation coefficient for a single run was 0.997 with most having 0.999. Agreement between repeat runs was usually better than 2%. A number of control experiments were carried out in conjunction with the kinetics determinations. (1) It was determined that the reaction product of the urethane prepolymer with dibutylamine was inert both to dibutylamine at the reaction temperature and to 2-propanol at ambient temperature. (2) The rate of reaction of dibutylamine with blocked polymer at ambient temperature was more than two orders of magnitude slower than the rate at 60°. (3) The continued unblocking of quenched reaction solutions at room temperature was more than two orders of magnitude slower than the rate of

(11) B. A. Dombrow, "Polyurethanes," 2nd ed, Reinhold, New York, N. Y., 1965, p 216.

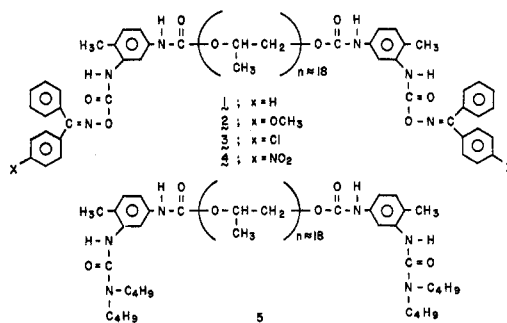


Figure 1.—Polymers synthesized for this investigation.

reaction at 60° before quenching. Additionally, the quenched rate was less than half the unquenched rate at ambient temperature.

Product Isolation and Identification.—To a 50-ml one-neck flask were added 45.05 g of a 75% solution of polymer 1 in toluene (33.79 g of polymer, 0.038 equiv) and 4.95 g (0.0384 equiv) of distilled dibutylamine. The solution was stirred magnetically and heated under reflux for 20 min. After cooling, 1 g of reaction mixture was chromatographed on an 8 × 300 mm column of alumina (Fisher 80-200 mesh). The column was eluted with acetone (16 ml) and then ether (6 ml) and 2-ml fractions were collected and concentrated. Fractions 1-3 contained polymer while 5-11 gave a white solid upon concentration. The combined solids were recrystallized from ether to give 75.3 mg (50% based on blocked polymer) of white crystals, mp 142-144°, identified as benzophenone oxime by peak matching of its ir spectrum with that of an authentic sample.

The remaining reaction mixture was allowed to stand at ambient temperature for 3 days after which time white solid had separated. The supernatant liquid was decanted and concentrated, and the concentrate was dissolved in CHCl₃. The ir spectrum of the CHCl₃ solution was equivalent to that of a solution of polymer 5 in the same solvent.

Results and Discussion

The blocked polymers used in this study are shown in Figure 1. Polymer 1 was subjected to some exploratory unblocking reactions,¹² which served as controls and to assign reaction stoichiometry. These experiments demonstrated that the reaction products were stable in the presence of dibutylamine, that the stoichiometry was 1 equiv of dibutylamine consumed/equiv of carbamate reacted, and that there was no competition for free isocyanate between dibutylamine and other N-H functions (urethane and urea) present. It was thus indicated that the rate of disappearance of amine would be an effective probe in determining reaction kinetics.

The reaction of polymers 1, 2, 3, and 4 with dibutylamine in toluene was followed by titrating quenched aliquots of reaction mixtures with aqueous HCl. The values of concentration of dibutylamine remaining were plotted in the usual manner for first-order reactions. A typical plot is shown in Figure 2, and Table II lists rate constants under various conditions. The fit of data to a first-order rate law is consistent with 1:1 stoichiometry provided that either the dibutylamine or the polymer is not kinetically active. Since it is impossible for the kinetics to be observed if the

(12) The details of these experiments, including method, results, and discussion as well as the graphical solution to the Eyring equation will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JOC-72-1500. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

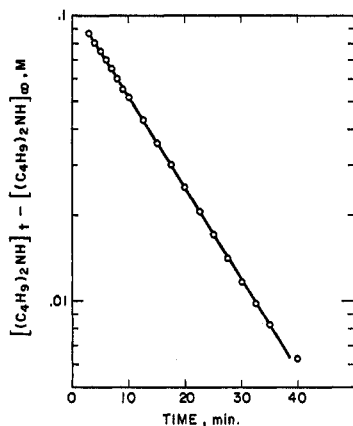


Figure 2.—Reaction of 1 with dibutylamine in toluene at 80.0° and 1:1 equivalent ratio.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR REACTION
OF POLYMERS WITH DIBUTYLAMINE

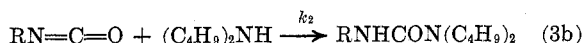
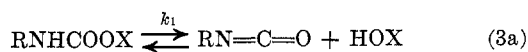
Polymer	Equiv ratio ^a	Temp, °C, ±0.1	10 ⁴ k, ^{b,c} sec ⁻¹
1	1:1	70	4.42 ± 0.07
1	2:1	70	4.16 ± 0.10
1	5:1	70	4.28 ± 0.004
1	10:1	70	4.49 ± 0.07
1	1:1	60	1.46 ± 0.04
1	1:1	80	12.96 ± 0.04
2	1:1	70	5.33 ± 0.03
3	1:1	70	3.67 ± 0.01
3	5:1	70	3.97 ^d
4	1:1	70	1.84 ± 0.003
1	0.5:1	80	11.7 ^{d,e}
1	0.5:1	70	4.15 ± 0.02 ^e
1	0.5:1	70	4.37 ^{d-f}

^a Dibutylamine:blocked isocyanate. ^b Average of at least two experiments with different initial concentrations. ^c Limits are ± average deviation of the mean. ^d Single experiment. ^e Using the special plot. See text. ^f Contained a molar amount of triethylamine equal to that of the dibutylamine.

polymer does not enter into the rate-determining step and since the rate constants are unaffected by both initial reactant concentration and ratio of amine to blocked isocyanate, the conclusion must be that the dibutylamine reacts with an intermediate generated by a unimolecular reaction of the blocked polymer. Such a reaction would be dissociation to the oxime and isocyanate-terminated prepolymer.

The rate constants for reaction of 1 with dibutylamine at three temperatures were used to solve the Eyring equation.¹² Assuming the transmission coefficient to be unity, the value of enthalpy of activation (ΔH^\ddagger) was found to be 24.8 ± 0.5 kcal mol⁻¹. The entropy of activation (ΔS^\ddagger) was -1.86 ± 0.8 cal deg⁻¹ mol⁻¹. The near-zero value of ΔS^\ddagger is consistent with a rate-determining unimolecular decomposition analogous to values found for unimolecular ester hydrolyses.¹³

Based on the foregoing data, a pathway for the unblocking reaction may be presented as shown in eq 3a and 3b. The blocked polymer dissociates to



(13) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

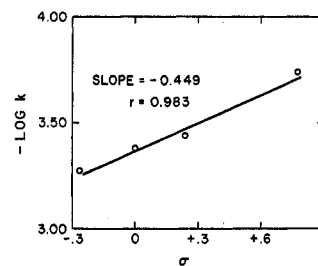


Figure 3.—Reaction of 1, 2, 3, and 4 with dibutylamine in toluene at 70° and 1:1 equivalent ratio. Plot of log k vs. the Hammett σ constant.

give an isocyanate and the blocking oxime, HOX. That this reaction is reversible seems quite reasonable when the blocking reaction and the high ΔH^\ddagger are considered. In a subsequent, fast reaction, dibutylamine adds to the isocyanate giving a urea. Provided that k_2 is larger than k_1 , the dissociation will be rate determining and the reaction will be first order. Since dibutylamine is known¹⁴ to be very reactive toward isocyanates, the $k_2 > k_1$ condition is easily met in this case. We have observed qualitatively that unblocking of 1 in the presence of 1-butanol is much slower than in the presence of dibutylamine. Since alcohols react more slowly with isocyanates than do amines,¹⁵ it is possible that $k_1 \geq k_2$ in the 1-butanol case. Under such circumstances, the reaction in eq 3 would follow second-order (or possibly higher) kinetics. This would result in an observed decrease in rate since the fractional change in concentration with time would no longer be time independent.

The pathway shown in eq 3 is the same as that proposed by previous workers for reaction of phenol blocked isocyanates with amines and carboxylic acids. However, there is a major difference in this case. Previously it has been found^{7,16} that electron-withdrawing substituents on the blocking agent facilitate the unblocking reaction. Considering polymers 2, 3, and 4 in our case it can be seen that the reverse is true. From a plot of the appropriate rate constants in Table II according to the Hammett equation,¹⁷ a ρ value of -0.45 was obtained as shown in Figure 3. This indicates that the reaction is slightly favored by electron-releasing substituents. The implication of these data is that, while the overall pathway of unblocking of oxime carbamates is similar to that for carbamates derived from phenols, the mechanism of the rate-determining dissociation is different. It should be noted that we performed no isomer separation on the substituted benzophenone oximes. The fact that smooth first-order kinetic behavior was found for polymers 2, 3, and 4 tends to confirm the report that both isomers of substituted benzophenone oximes give the same derivative when treated with phenyl isocyanate.¹⁸

An interesting test for overall reaction pathway was available for this reaction. We found that straightforward kinetics were demonstrated by all reactions where the number of equivalents of dibutylamine present was either equal to or greater than the number

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(17) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(18) O. L. Brady and R. P. Mehta, *J. Chem. Soc.*, **125**, 2297 (1924).

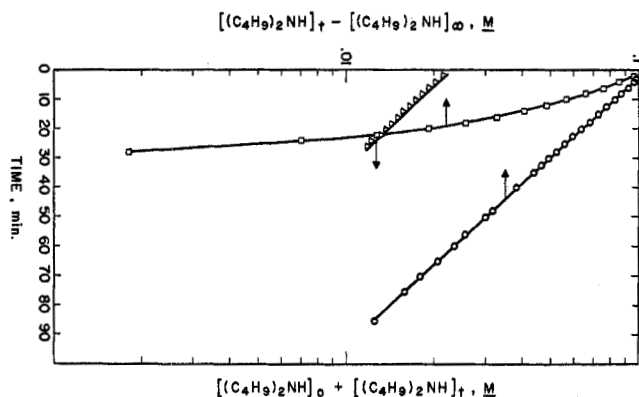


Figure 4.—Reaction of 1 with dibutylamine in toluene at 70°C: O, $[\text{polymer}]_0 = [\text{amine}]_0$; □, $2[\text{polymer}]_0 = [\text{amine}]_0$; Δ, $2[\text{polymer}]_0 = [\text{amine}]_0$. Plot of $\log([\text{amine}]_t - [\text{amine}]_\infty)$ (O, □) or $\log([\text{amine}]_t + [\text{amine}]_0)$ (Δ) vs. time.

of equivalents of carbamate. When carbamate concentration exceeded that of the amine, however, the fractional change in concentration of amine with time increased markedly after ~50% reaction. A kinetic analysis of the pathway in eq 3 showed that, in the case where the number of equivalents of blocked isocyanate was twice that of the amine, an unusual, first-order-like variation of concentration with time would be observed. Specifically in this case, a plot of \log of the sum of initial and remaining amine concentrations vs. time would give an initial straight line. The slope of such a line would be equal to the slope of the customary first-order plot for the reaction at the same temperature where the dibutylamine concentration was equal to or greater than the carbamate concentration.

This criterion was applied and the results at 70°C are shown in Figure 4. As can be seen, a slope similar to that for a reaction where carbamate/amine = 1 was obtained. Interestingly, the effect was independent of absolute concentration, as the same line was obtained with initial polymer concentrations 0.121 or 0.242 normal. Additionally, when an amount of triethylamine equal to the concentration of dibutylamine was added, no effect on rate was observed. If the amine were involved in catalysis of the rate-determining dissociation, one would expect to observe a rate enhancement by the triethylamine in this otherwise amine-deficient system. The above experiment thus substantiates the dissociation-addition pathway (eq 3) and also provides a clue to the manner in which this unblocking differs from those previously studied.

The requirements for the rate-determining transition state in the present reaction follow: it must be unimolecular, resulting in dissociation; it must not be attainable by (or be of much higher energy for) phenol blocked isocyanates; it is not subject to base catalysis despite the necessary proton transfers. These limitations seem to indicate an intramolecular activated complex. Examination of the transition state in Figure 5 shows that the nitrogen lone pair of the azomethine moiety is capable of interaction with the

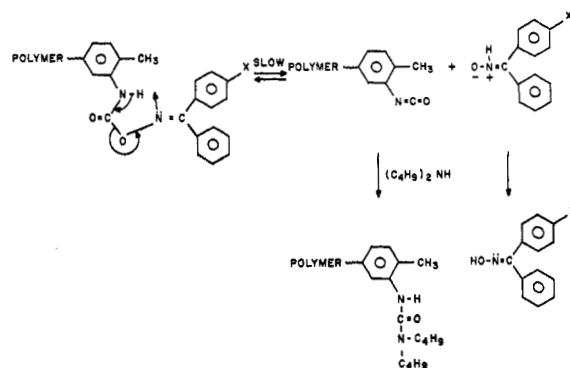


Figure 5.—Mechanism of unblocking in the presence of dibutylamine.

urethane hydrogen atom. This cyclic structure cannot form in the case of carbamates derived from phenols unless the aromatic ring participates which is energetically prohibitive under the conditions of this reaction. The intramolecular, cyclic nature of the postulated transition state is consistent with the insensitivity of the rate to added triethylamine and with the observed first-order kinetics. Since the azomethine nitrogen atom must act as a base in this reaction, electron-releasing substituents on the oxime moiety would increase the base strength and thus increase the rate. The lone pair is far removed from and not conjugated with the substituent, X, however, and one would thus expect a relatively small electronic effect. The transition state is pictured in Figure 5 proceeding to isocyanate and a relatively unstable tautomer of the oxime.

Molecular models show that the geometry necessary to form the cyclic transition state is probably not that of the ground state for the molecule. It may be attained, however, without greatly straining any bond. The steric hindrance to approach of a dibutylamine molecule is considerable, and consequently the cyclic transition state proposed is of lower energy than would be one which required higher order kinetics. There is an alternative unimolecular transition state for this reaction where proton transfer occurs *via* a four-center process. This is similar to the transition state usually pictured^{7a} for uncatalyzed carbamate formation from an alcohol and an isocyanate. For the molecule at hand, the five-center geometry seems more favorable. Further, the reverse of alcohol addition is alcohol unblocking. Since alcohol unblocking has opposite electronic requirements,⁷ we must conclude that a four-center transition state has a higher energy of activation than does the postulated transition state for unblocking of oxime carbamates.

Registry No.—Dibutylamine, 111-92-2.

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