The Thermal Dissociation of Aryl Carbanilates in Glyme

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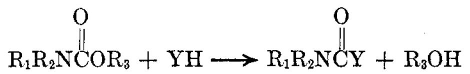
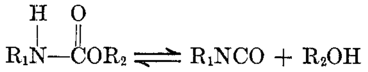
Members of a series of meta- and para-substituted phenyl carbanilates were shown to undergo a rapid reversible dissociation in glyme. The equilibrium constants for this dissociation were measured at temperatures between 90.4 and 150° (50 and 90.4° in the case of *p*-nitrophenyl carbanilate). The reaction followed the Hammett equation and gave the positive ρ values of 1.49–1.66. The significance of the thermodynamic parameters and Hammett correlations is discussed.

It has been known for some time that carbamates undergo an ester interchange reaction with alcohols, amines, and other active hydrogen compounds.[1–5]

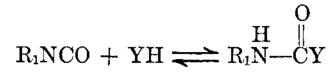


$$R_1R_2N\overset{O}{\overset{\|}{C}}OR_3 + YH \longrightarrow R_1R_2N\overset{O}{\overset{\|}{C}}Y + R_3OH \tag{1}$$

There are several different pathways by which this reaction may proceed, and the choice of a particular pathway appears to depend on the nature of the carbamate, the catalyst, and the temperature. In the alkoxide ion catalyzed transesterification of alkyl N,N-disubstituted carbamates (reaction 1, R_1, R_2, R_3 = alkyl; Y = RO), evidence has been presented for a carbonyl addition intermediate.[2b] In the case of monosubstituted carbamates (reaction 1, R_2 = H) an alternate pathway is available. These compounds may dissociate at elevated temperatures, usually with acid or base catalysis, to form isocyanate and alcohol,[6–9] and the ester interchange may proceed by a two-step process. Mukaiyama and coworkers[3] have carried out kinetic studies on the ester interchange reaction of substituted benzyl carbanilates with several active hydrogen-containing compounds at temperatures of 130–170°, and they assume a mechanism represented by eq 2 and 3.



$$R_1\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}OR_2 \rightleftharpoons R_1NCO + R_2OH \tag{2}$$



$$R_1NCO + YH \rightleftharpoons R_1\overset{H}{N}-\overset{O}{\overset{\|}{C}}Y \tag{3}$$

Pseudounimolecular rate constants were reported.[10] The rate constants for the reaction of the substituted benzyl carbanilates with ethanolamine at 150° followed the Hammett relationship and gave a ρ value of +0.538. The substitution was in the anilide ring of the benzyl carbanilate.

Both dissociation (reaction 2) and ester interchange (reaction 1) are facile in the case of aryl *N*-arylcarbamates,[2] and can take place either in the presence or absence of added catalyst depending on the temperature. Tartakovskaya and coworkers[9] studied the decomposition temperatures of a number of solid aryl carbanilates suspended in mineral oil. These temperatures, the lowest at which phenyl isocyanate could be identified in an infrared spectrum, ranged from 100° for *p*-nitrophenyl carbanilate to 150° for *p*-tolyl carbanilate. In dioxane solution, *p*-nitrophenyl carbanilate has been reported to dissociate at room temperature with an equilibrium constant of about 2×10^{-3} mol/l.[7] The dissociation was catalyzed by trimethylamine.

The rates of aminolysis of aryl carbanilates with aniline in dioxane, catalyzed by triethylamine at 80°, were studied by Furuya and coworkers.[4] The reactions of phenyl, *p*-tolyl, and *p*-methoxyphenyl carbanilates with aniline were first order in urethane and first order in triethylamine. Evidence was presented that suggested the formation of a cationic complex as the rate-determining step. *p*-Chlorophenyl carbanilate and *p*-nitrophenyl carbanilate gave more complex kinetics, and the latter also underwent aminolysis in the absence of triethylamine.

Sal'nikova and coworkers[5] have studied the ester interchange between aryl carbanilates and 1-hexanol in *o*-dichlorobenzene. The reactions were carried out without added catalyst at 160–180°. Phenyl isocyanate was identified as an intermediate, but the overall ester interchange was interpreted as a bimolecular nucleophilic displacement involving a carbonyl addition intermediate. Second-order rate constants were reported for this reaction, which was said to compete with the dissociation of aryl carbanilates.

The evidence bearing on the mechanisms of the carbamate ester interchange presents a rather confusing picture. As part of an effort to clarify the mechanism of the overall ester interchange reaction, we have studied the thermal dissociation of aryl carbanilates in ethylene glycol dimethyl ether (glyme). The dissociation was very rapid and reversible and did not require the addition of a catalyst. Phenyl carbanilate (0.09 mol/l. in glyme) dissociated to the extent of 23% at 90.4° and

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[1] J. H. Saunders and K. C. Frisch "Polyurethane Chemistry and Technology," part I, Interscience, New York, N. Y., 1963, pp 103–112.

[2] (a) N. G. Gaylord and C. E. Sroog, *J. Org. Chem.*, **18**, 1632 (1953); (b) N. G. Gaylord, *ibid.*, **25**, 1874 (1960).

[3] (a) T. Hoshini, T. Mukaiyama, and H. Hoshino, *J. Amer. Chem. Soc.*, **74**, 3097 (1952); (b) T. Mukaiyama and T. Matsunaga, *ibid.*, **75**, 6209 (1953); (c) T. Mukaiyama and Y. Hoshino, *ibid.*, **78**, 1946 (1956); (d) T. Mukaiyama and M. Iwanami, *ibid.*, **79**, 73 (1957).

[4] Y. Furuya, S. Goto, K. Itoho, I. Urasaki, and A. Morita, *Tetrahedron*, **24**, 2367 (1968).

[5] G. A. Sal'nikova, Ya. A. Shmidt, and Yu. I. Volodarskaya, *Dokl. Akad. Nauk SSSR*, **181**, 669 (1968).

[6] N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Amer. Chem. Soc.*, **78**, 4358 (1956).

[7] K. D. Kopple, *ibid.*, **79**, 6442 (1957).

[8] E. Dyer and G. C. Wright, *ibid.*, **81**, 2138 (1959).

[9] A. M. Tartakovakaya, A. A. Blagonravova, and Yu. A. Strepikheev, *Lakokrasoch. Mater. Ikh. Primen*, (6) 1 (1967); (5) 6 (1968) [*Chem. Abstr.*, **68**, 59196a (1968); **70**, 37334h (1969)].

[10] These workers[3] assumed that reaction 2 was the rate-determining step and therefore that their first-order rate constants referred to the rate of this dissociation. If this were the case, then the first-order rate plots should have an intercept at zero time equal to the logarithm of the initial amine concentration. The published rate plots for the reaction of *N*-*p*-nitrophenyl benzyl carbamate with ethanolamine in benzyl alcohol[3d] have intercepts smaller than this value, and the extrapolated concentration of amine at zero time decreases with decreasing temperature. This behavior strongly suggests that an intermediate was present in high concentration and is inconsistent with reaction 2 as the rate-determining step. Reaction 3 may have been rate determining in which case the observed rate constant would be equal to K_2k_3X, where K_2 is the equilibrium constant for reaction 2, k_3 is the second-order rate constant for reaction 3, and X is the ratio of ethanolamine concentration to benzyl alcohol concentration. The value of X would be constant since both reagents were present in excess.

63% at 150°. Equilibrium was reached within 10 min at 90.4° and within 2 min at 150°.

Experimental Section

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Carbon–hydrogen analyses were performed by Crobaugh Laboratories, Cleveland, Ohio. Infrared absorption measurements were made with a Beckman IR-12 double-beam spectrophotometer, using a 0.1-mm Irtran cell.

Materials.—Aryl carbanilates were prepared from phenyl isocyanate and the corresponding phenols in benzene solution, using a catalytic amount of pyridine. The resulting colorless solids were recrystallized from hexane in a Soxhlet apparatus and dried under vacuum. The melting points and carbon–hydrogen analyses are shown in Table I.

TABLE I

MELTING POINTS FOR SUBSTITUTED PHENYL CARBANILATES

Compd[a]	Registry no.	Mp, °C	Lit. mp, °C
Unsubstituted	4930-03-4	126–127	123[b]
p-CH_3	16323-13-0	111.5–112.5	113[b]
p-F	29913-14-2	150–151	
m-F	29913-15-3	114–115.5	
p-Cl	16400-09-2	144–146	139,[b] 138.5[c]
p-Br	16323-16-3	142.5–144	138[c]
p-OCH_3	19219-48-8	135–137	135[c]
m-OCH_3	21123-19-3	120–122.5	123–124[d]
p-NO_2	6320-72-5	153–155	147[b] 149–150[e] 93.5–94[c]

[a] Satisfactory analyses (±0.4%) for C and H were provided for this compound: Ed. [b] Reference 4. [c] Reference 9. [d] M. T. Leffler and E. J. Matson, *J. Amer. Chem. Soc.*, **70**, 3439 (1948). [e] Reference 7.

Solvent purification and solution preparation were carried out in a self-contained apparatus under an atmosphere of dry prepurified nitrogen. The glyme was distilled once from sodium ribbon and again from lithium aluminum hydride. Both distillations used an 86-cm vacuum-jacketed column operated at a reflux ratio of 10:1. Only the center cut was retained in each distillation. The distillate was then drained into a volumetric flask containing the requisite amount of aryl carbanilate. This flask was provided with a magnetic stirrer for mixing and with a Teflon stopcock and exit tube for filling the reaction vessels. The distillation receiver and volumetric flask were dried before starting the distillation by heating with a flame in a current of dry nitrogen.

Solutions of phenyl isocyanate, for use in calibration of absorbance, were prepared by distilling phenyl isocyanate into a volumetric flask under dry nitrogen. The flask was then weighed, transferred to the distillation receiver described above, and filled with freshly purified glyme under nitrogen.

Procedure.—The reaction was carried out in sealed Pyrex tubes of 2.2-ml capacity charged with 1 ml of solution. Each tube was dried before filling by heating with a flame in a current of dry nitrogen, and the nitrogen current was maintained until the tube was filled. After each tube was filled, it was immediately sealed under vacuum and stored in a Dry Ice–acetone bath.

The reaction was carried out in a thermostated oil bath which maintained the stated temperatures within 0.1°. Tubes were withdrawn at intervals, cooled in a Dry Ice–acetone bath, warmed to room temperature, and opened. The infrared cell was filled and the absorbance measured as rapidly as possible. Typically the isocyanate absorbance was measured within 6 min after removing the reaction tube from the oil bath, and the urethane carbonyl absorbance was measured 1 min later. In all runs involving phenyl carbanilate, the infrared spectrum of the solution was scanned between 1500 and 4000 cm^{-1} after the initial absorbance measurements were made. Extraneous peaks were not observed. The reversal of the reaction took place slowly within the infrared cell. In one case, involving an equilibrium sample of phenyl carbanilate, the concentration of isocyanate decreased to 87.5% of its initial value after 40 min in the cell, while the concentration of phenyl carbanilate increased correspondingly.

The concentration of phenyl isocyanate was determined from its strong, sharp absorbance at 2262.5 cm^{-1}, after subtracting the solvent absorbance of 0.129–0.131 absorbance units. The solvent absorbance was rechecked periodically. The isocyanate absorbance was calibrated at ten concentrations covering the range of interest and followed Beer's law with an extinction coefficient of 1314 ± 48. The concentration of phenyl carbanilate was determined from its carbonyl absorbance at 1757 cm^{-1}, after subtracting the solvent absorbance of 0.056–0.060 absorbance units. A separate calibration chart was prepared for each aryl carbanilate. The absorption maxima and extinction coefficients are shown in Table II. *p*-Nitrophenyl carbanilate underwent dissociation within the infrared cell, and so an accurate calibration chart could not be prepared.

TABLE II

INFRARED MAXIMA AND EXTINCTION COEFFICIENTS FOR SUBSTITUTED PHENYL CARBANILATES

Compd	ν_{max}, cm^{-1}	ϵ_{max}[a]	n[b]
Unsubstituted	1757	1004 ± 10	8
p-CH_3	1755	1060 ± 5	5
p-F	1757	1111 ± 17	5
m-F	1759	1104 ± 25	5
p-Cl	1755.5	1085 ± 16	8
p-Br	1754	957 ± 5	4
p-OCH_3	1753	1015 ± 38	5
m-OCH_3	1757	1055 ± 10	5
p-NO_2	1759		

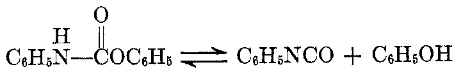
[a] By least-squares correlation including the origin ± standard deviation in slope. [b] Number of measurements, not including the origin.

The concentrations of phenyl isocyanate and aryl carbanilate were measured at various time intervals. The results of a typical run are shown in Figure 1. In all cases, the concentration of phenyl isocyanate rose rapidly and quickly reached an equilibrium value, while the aryl carbanilate concentration decreased correspondingly to an equilibrium value. The equilibrium concentration was taken as the concentration which did not change during three measurements over a period of at least 30 min. The time required to reach equilibrium was about 10 min in most cases. The shortest time was 2 min for phenyl carbanilate at 150°, and the longest time was 45 min for *p*-nitrophenyl carbanilate at 50°. A reaction requiring 2–10 min (Figure 1) is much faster than it appears to be, since most of the reaction occurs during the period necessary to bring the sample to thermal equilibrium in the constant temperature bath.

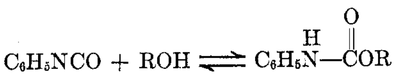
The equilibrium constants were calculated as the square of isocyanate concentration divided by the urethane concentration. In the case of *p*-nitrophenyl carbanilate only the isocyanate concentration was measured.

Results and Discussion

Under certain conditions, it appears likely that the exchange reaction between phenyl carbanilate and alcohols may occur in two major steps, as shown in eq 4 and 5.



$$C_6H_5\overset{H}{N}\text{—}\overset{\overset{O}{\|}}{C}OC_6H_5 \rightleftharpoons C_6H_5NCO + C_6H_5OH \qquad (4)$$



$$C_6H_5NCO + ROH \rightleftharpoons C_6H_5\overset{H}{N}\text{—}\overset{\overset{O}{\|}}{C}OR \qquad (5)$$

The study of these reactions independently should provide valuable information concerning the overall exchange reaction. Reaction 5 has been studied extensively. It is relatively slow in ether solvents and approximates second-order kinetics. The apparent second-order rate constant is reported as 1.33×10^{-6} l. mol^{-1} sec^{-1} for 0.15 *M* butanol–phenyl isocyanate at 25° in dioxane, and the reaction is still slower in diglyme.[11] Reaction 4, on the other hand, is very fast relative to the overall ester interchange reaction. Preliminary experiments with octanol and phenyl carbanilate in glyme[12] suggest that the overall transesterification (reactions 4 and 5) requires several hours to reach completion at 150°. On the other hand, reaction 4 reaches equilibrium within 2 min. We were unable to determine the kinetic order of reaction 4 because of the time necessary for the mixture to reach thermal equilibrium. Furuya and coworkers[4] have observed an induction period of 200 min for the uncatalyzed reaction of *p*-nitrophenyl carbanilate with aniline in dioxane at 80°. We have not observed induction periods in the present work, and there is no evidence for inhibition phenomena in reaction 4. The precise mechanism of this reaction remains in doubt.

The equilibrium constants and thermodynamic parameters for the dissociation of aryl carbanilates are shown in Table III. Most of the $\Delta H°$ and $\Delta S°$ values are of the order of magnitude expected for a thermal dissociation, but the $\Delta S°$ value for *p*-nitrophenyl carbanilate is surprisingly high. This value possibly may reflect a high degree of association of the starting urethane in the solvent. It should be noted that the log *K vs.* $1/T$ correlation for *p*-nitrophenyl carbanilate was obtained over a different temperature range than those for the other aryl carbanilates and is also subject to a greater degree of uncertainty. Extrapolation gives an equilibrium constant of about 2×10^{-4} mol l.$^{-1}$ for the dissociation of *p*-nitrophenyl carbanilate in glyme at 25°, as compared to a value of about 2×10^{-3} mol l.$^{-1}$ reported by Kopple[7] for the same dissociation in dioxane at room temperature catalyzed by trimethylamine.

TABLE III

DISSOCIATION OF SUBSTITUTED PHENYL CARBANILATES IN GLYME

Substituent[a]	*K*, mol. l.$^{-1}$ × 10^2 150°	125°	100°	90.4°	$\Delta H°$,[b] kcal	$\Delta S°$,[b] eu
H[c]	9.39	3.48	1.08	0.629	13.9 ± 0.1	28.0
H[d]			1.05			
p-CH_3	5.67	1.93	0.542	0.277	15.4 ± 0.2	30.7
p-F	10.1	3.20	0.914	0.429	15.9 ± 0.2	33.2
m-F	33.1	11.0	3.19		14.7 ± 0.01	32.5
p-Cl	13.1	5.66	1.82	0.960	13.4 ± 0.4	27.7
p-Br	14.6	4.56	1.58	1.01	13.6 ± 0.3	28.3
p-OCH_3	3.91	1.26			15.1	29.3
m-OCH_3	13.4	4.76	1.43	0.890	14.0 ± 0.03	29.0
p-NO_2				11.1[e]	21.3 ± 1.4	54.7

[a] Initial concentration 0.075 mol/l. except where otherwise noted. [b] From least-squares correlation of log *K vs.* $1/T$. Standard deviations in slope are shown. [c] Initial concentration 0.09 mol/l. [d] Initial concentration 0.0831 mol/l. [e] $K \times 10^2$ was 4.75 at 75°, 1.02 at 60°, and 0.306 at 50°.

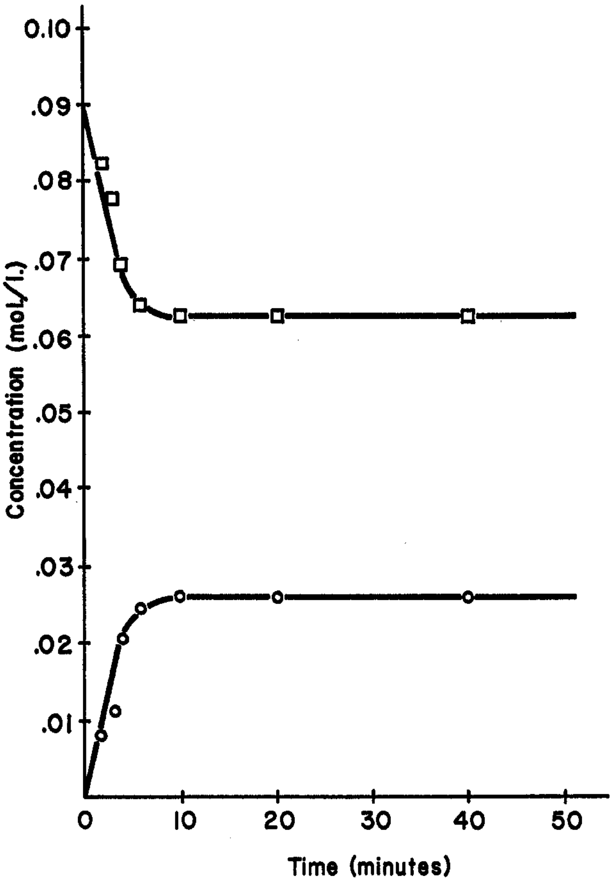


Figure 1.—Dissociation of phenyl carbanilate at 100°. Concentration of phenyl isocyanate (circles) and phenyl carbanilate (squares) *vs.* time.

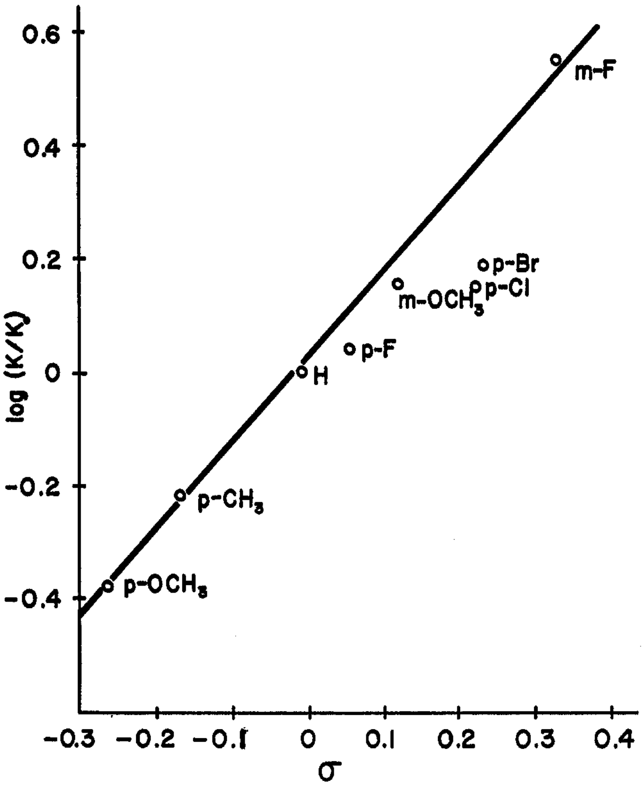


Figure 2.—Dissociation of aryl carbanilates at 150.0°. Correlation of equilibrium constants with Hammett σ values.

Electron-withdrawing meta and para substituents on the phenolic ring increase the extent of dissociation, and electron-releasing substituents decrease the extend of dissociation. The reaction approximately followed the Hammett equation (Figure 2). The points for para halogen substituents fell below the line at all temperatures. The values of ρ, estimated by least-squares correlation omitting the para halogens, were +1.66 at

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(11) A. E. Oberth and R. S. Bruenner, *J. Phys. Chem.*, **72**, 845 (1968).

(12) A. B. Lateef, unpublished results.

90.4°, +1.49 at 100°, +1.53 at 125°, and +1.50 at 150°.

The values of ρ in the present case are rather similar to the ρ value of +1.63 reported by Furuya and coworkers[4] for the aryl carbanilate–aniline interchange reaction in dioxane. However, there are obvious differences between the present products and the transition state postulated[4] for the interchange. A ρ value of +0.272 was reported for the second-order rate of the ester interchange between aryl carbanilates and 1-hexanol in *o*-dichlorobenzene.[5] The mechanism of this reaction presumably did not involve dissociation, and in any case the effect of substituents on the equilibrium constant for dissociation in dichlorobenzene may not be similar to that in ether solvents.

Previous workers have interpreted the positive ρ values in urethane interchange reactions in terms of an increase of the positive charge on carbonyl carbon[4] or amide nitrogen[3d] caused by electron-withdrawing substituents. In the present case, the data in Table III suggest that any correlation between log K and σ would result from a balance between the enthalpies and entropies of formation, solution, and association in the reactants and products. Since neither $\Delta H°$ nor $\Delta S°$ for the dissociation appears to correlate with σ, it would be difficult to interpret a linear free-energy correlation in terms of internal electronic effects within the urethane and phenol molecules.

A large number of reactions are known in which a Hammett linear free-energy correlation appears to exist, but in which both $\Delta H°$ and $\Delta S°$ change in a nonlinear manner with changes in σ.[13] In such reactions there appears to be a reasonable linear correlation between $\Delta H°$ and $\Delta S°$. These correlations have been interpreted in various ways,[13–16] but their significance is not established. Recently an effort has been made to rationalize correlation between enthalpy and entropy of activation in a qualitative manner, by reference to the effect of σ on the enthalpy and energy of solvation.[17] Such a rationalization would be difficult to apply to the present case, since there is no discernable trend in the value of log K with increasing $\Delta H°$. It has been suggested[18,19] that most or all of the linear enthalpy–entropy correlations reported in the literature are fallacious, at least when these correlations are based in kinetic measurements. By this interpretation, such correlations are fundamentally derived from experimental errors in the original measurements and from improper statistical treatment of the data.

The present equilibrium studies provide a basis for the further study of rates and mechanisms in the transesterification of aryl carbanilates. The mechanisms of this reaction may change fundamentally with changes in temperature, solvent, and catalyst. The reaction of alcohols with isocyanate (reaction 5) is much faster in alcohol or hydrocarbon solvents than in ether solvents,[12] and the rate changes much less rapidly with temperature than does the equilibrium constant for dissociation (reaction 4). The activation energy for the reaction of phenyl isocyanate with 1-butanol in toluene was reported as 3.1 kcal mol^{-1} at 24–40°.[20] The rate of bimolecular nucleophilic attack may also be very sensitive to solvent, catalyst, and temperature. In order to examine the above factors more closely, we are presently investigating urethane dissociation equilibria in other aprotic solvents, and the kinetics of the urethane transesterification reaction in ether and alcohol solvents.

Acknowledgment.—This work was supported by the U. S. Army Research Office, Durham, to whom acknowledgment is gratefully given.

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[14] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

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[17] J. T. Burns and K. T. Leffek, *Can. J. Chem.*, **47**, 3725 (1969).

[18] R. C. Peterson, J. A. Mashgray, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961).

[19] O. Exner, *Nature*, **201**, 488 (1964).

[20] J. Burkus and C. F. Eckert, *J. Amer. Chem. Soc.*, **80**, 5948 (1958).