with $^1/_8''$ NaF pellets. Twenty-eight grams (0.21 mole) of $CF_3N{=}CF_2$ and 44 g. (0.23 mole) of CF_3SF_5 were run through a nickel tube filled with $^1/_8''$ NaF pellets at 519° and 1 atm. pressure at a mass rate of 0.18 g./min. The materials boiling below −35° and above −12° were removed by fractionation and retained. That boiling between −35 and −12° was further augmented by 9 g. of CF_3SF_5 and passed through the reactor at 540°. The products of both trials were fractionated and were essentially: 8 g. of C_2F_6, 23 g. of SF_4 (and other sulfur fluorides), 4.5 g. of unreacted $CF_3N{=}CF_2$ (from NH_3 evolved on hydrolysis), 10 g. of unreacted CF_3SF_5, 23.5 g. of $(CF_3)_3N$ and 4 g. of unidentified material with a boiling range above 0°. The $(CF_3)_3N$ was obtained from the fractionation at temperatures between −11.3 and −10.7°. The m.p. was −114.7 ± 0.5°. The v.p. curve fits the equation

$$\log_{10} p_{\text{mm.}} = -\frac{1250}{T,\ ^\circ\text{K.}} + 7.61$$

well between −80 and −10°. The calculated b.p. is −10.9°, H_v = 5680 cal./mole and Trouton's constant 21.6. The sharp m.p. indicated that it was a pure compound and not a mixture of isomers. NMR spectrum analysis[11] confirmed the structure as that required for $(CF_3)_3N$. It showed only a single F^{19} resonance component located at $\delta = +0.3$ with respect to benzotrifluoride, $\delta = 10^5(\text{Hr} - \text{Hc})/\text{Hc}$. At a later date this was reconfirmed by a comparison infrared spectrum with material from an independent source.[12]

Attempted Reaction with $(CF_3)_2SF_4$ and $CF_3N{=}CF_2$.—Using the same equipment, 24 g. (0.1 mole) of $(CF_3)_2SF_4$ and 13.5 g. (0.1 mole) of $CF_3N{=}CF_2$ were allowed to react at 520°, one atmosphere pressure and a mass flow rate of 0.15 g./min. Equimolar concentrations were obtained by bubbling the lower boiling reactant, $CF_3N{=}CF_2$, through the higher boiling one at a temperature of about 4° (v.p. 400 mm.) before passing them into the reactor. After the trial, 96% of the $CF_3N{=}CF_2$ was recovered unreacted while 2.0 g. of CF_4, 7.5 g. of C_2F_6, 5.5 g. of SF_4 and 4.5 g. of CF_3SF_3 were found. Almost no $(CF_3)_2SF_4$ was recovered but some material with a greater molecular weight, *viz.*, 253 to 285 was found. From the products recovered and identified, it appeared that the reactions involved were two simultaneous disproportionations as indicated by the equations

$$(CF_3)_2SF_4 \longrightarrow C_2F_6 + SF_4 \quad 65\%$$

$$(CF_3)_2SF_4 \longrightarrow CF_3SF_3 + CF_4 \quad 35\%$$

Trifluoromethylsulfur trifluoride is a derivative of SF and like it is completely destroyed by aqueous base. It was recovered from fractionation at −6 to −5° (reported −7°).[13]

Anal. Calcd. for CSF_6: F, 72.2; S, 20.3; mol. wt., 158. Found: F, 73.2; S, 18.8; mol. wt., 158.

CF_3SF_3 will attack Pyrex glass slowly at room temperature over a period of months, apparently forming high molecular weight solid silicon fluorides (dec. *circa* 300°).

Reaction of $CF_3N{=}CF_2$ with $C_2F_5SF_5$.—In order to attempt to get greater conversion in this reaction, it was performed in a 500-ml. stainless steel pressure reaction vessel (Hoke) with a pressure gage and valve attached. Thirteen grams (0.1 mole) of $CF_3N{=}CF_2$ and 24.5 g. (0.1 mole) of $C_2F_5SF_5$ were condensed into the vessel, which was heated in a vertical furnace. Temperatures were observed by placing a chromel-alumel thermocouple in the wall of the furnace. Heat was applied slowly, so that the average temperature rise was 2°/min. The slope of the *P vs. T* curve was zero or negative between 372 and 384° indicating a reaction in this temperature range at 12 atm. Above this temperature the pressure rose gradually with temperature and the heating was discontinued. The products were removed from the vessel and examined. In the fractionation, 3.5 g. of C_2F_6, 11.5 g. of SF_4, 5 g. of $CF_3N{=}CF_2$, 6 g. of an azeotrope partly destroyed by dilute aqueous base, b.p. −8 to −6°, mol. wt. 169–172, and 7.5 g. of material boiling at 20.5° identified as $(CF_3)_2NC_2F_5$, mol. wt. 268–272 (calcd. 271) were isolated.[3] Curiously, no C_4F_{10} was detected. Losses and intercuts accounted for the rest of the material. $(CF_3)_2NC_2F_5$ was subjected to NMR spectrum analysis[11] and the resultant lines corresponded to the CF_2, $C{=}CF_3$ and $N(CF_3)_2$ peaks found in pure samples of $(CF_3)_3N$ and $(C_2F_5)_3N$. There was no evidence of any $CF_3NF(C_3F_7)$ isomer present. Again based on the unrecovered amount of $CF_3N{=}CF_2$ the reaction yield to produce $(CF_3)_2NC_2F_5$ was 46%.

Acknowledgments.—The author wishes to thank the Chemistry Branch of the Office of Naval Research for its support of this work. Our thanks are extended to Dr. H. S. Gutowsky and Mr. Apollo Saika for performing and interpreting the Nuclear Magnetic Resonance spectra cited in this work. My profound thanks to my colleague Dr. J. A. Young for his contribution of a sample of perfluoro-2-azapropene and to Dr. T. J. Brice for physical data on perfluorobutylsulfur pentafluoride.

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[11] Analysis and interpretation made by Dr. H. S. Gutowsky and Mr. Apollo Saika, Dept. of Chemistry, Univ. of Illinois, Urbana Ill.; more detailed NMR results to be published by them at a later date.

[12] Sample obtained from Dr. J. A. Young, University of Florida.

[13] E. A. Tyczkowski and L. A. Bigelow, THIS JOURNAL, **75**, 3523 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity. XI. Hydrazinolysis of Ethyl Acetate

BY RICHARD A. FERREN, JOHN G. MILLER AND ALLAN R. DAY

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The effects of a number of hydroxylated solvents on the hydrazinolysis of ethyl acetate have been determined. In all cases increases in reaction rates were observed.

The reaction of ethyl acetate with hydrazine, as catalyzed by aliphatic alcohols, has been investigated. The effects of these solvents on the rates of hydrazinolysis have been determined and the energies and entropies of activation for the reactions have been calculated. These reactions are similar in many ways to the ammonolyses and aminolyses of esters which have been reported earlier.[1] The previous work showed that the effects of solvents on reaction rates often are quite complex. It was hoped that a quantitative study of the action of certain solvents on the hydrazinolysis of ethyl acetate would produce new and useful information concerning these effects.

In order to study the action of hydroxylated solvents on the rates of hydrazinolysis, the following solutions of reactants and solvents were used:

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[1] (a) M. Gordon, J. G. Miller and A. R. Day, THIS JOURNAL, **70**, 1946 (1948); **71**, 1245 (1949); (b) T. A. Koch, J. G. Miller and A. R. Day, *ibid.*, **75**, 4664 (1953); (c) F. H. Wetzel, J. G. Miller and A. R. Day, *ibid.*, **75**, 953 (1953); (d) E. McC. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950); **73**, 5393 (1951).

I, 2.5 *M* water, 1 *M* ethyl acetate, 5 *M* ethyl alcohol, 5 *M* alcohol, 2 *M* hydrazine and dioxane as diluent. II, 2.5 *M* water, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and dioxane as diluent. III, 2.5 *M* water, 1 *M* ethyl acetate, 5–13.5[2] *M* ethyl alcohol, 2 *M* hydrazine and dioxane as diluent. IV, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and benzene as diluent. V, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and cyclohexane as diluent.

Many of the earlier ammonolysis studies carried out in this Laboratory were made with aqueous solutions so that both ammonolysis and hydrolysis occurred. In the present study, the amount of water present was so low and the hydrazinolysis reaction so rapid that competing hydrolysis was not observed.

Experimental

Apparatus.—Burets, pipets, volumetric flasks and thermometers were carefully calibrated. The constant temperature bath maintained a given temperature within ±0.01°.

Reagents.—1,4-Dioxane, ethyl acetate, methyl alcohol, ethyl alcohol, ethylene glycol and propylene glycol were purified as described in previous papers.[1] The higher molecular weight alcohols were dried over calcium oxide and fractionally distilled. Only those fractions having the correct boiling points and refractive indices were used.

Hydrazine hydrate was used as obtained from Matheson, Coleman and Bell. It is listed as 99–100% hydrazine hydrate. The exact amount of hydrazine present was determined by the usual acid–base titration method. The hydrate was used only in those solutions where the presence of water was desired.

Anhydrous hydrazine was obtained from 95% hydrazine by distilling several times from excess barium oxide, b.p. 113–113.5°. It was found by analysis to be 99.9% pure.

Benzene, analytical grade, was distilled over sodium, b.p. 80°, $n^{25}\text{D}$ 1.4974.

Cyclohexane, analytical grade, was distilled over sodium, b.p. 80–81°, $n^{25}\text{D}$ 1.4237.

Procedure.—Concentrated solutions, corresponding to solutions I to V, containing all of the reagents except ethyl acetate, were prepared. Aliquots were removed as needed, ethyl acetate added, the solution diluted to the desired volume with the appropriate diluent and the resulting solution used for the rate experiment. An example of this procedure is given below for the preparation and use of solution I.

Preparation and Procedure for the Use of Solution I (2.5 *M* water, 1 *M* ethyl acetate, 5 *M* ethyl alcohol, 5 *M* alcohol, 2 *M* hydrazine, and dioxane as diluent).—The strength of the concentrated solution, to be prepared, was determined by the number of experiments to be carried out. In this particular case 500 ml. of a solution was prepared which contained 5 moles of water, 10 moles of ethyl alcohol, 4 moles of hydrazine and dioxane as diluent. After thoroughly mixing, a 50-ml. aliquot was transferred to a 100-ml. volumetric flask. The alcohol to be used in addition to the ethyl alcohol was added in sufficient amount to make the solution 5 *M*. The solution was diluted with dioxane to about 85 ml. and 0.1 mole of ethyl acetate added from a 10-ml. buret. The volume of ethyl acetate to be added was determined from a plot of temperature against ml. of ethyl acetate per 0.1 mole. Dioxane was then added to bring the volume to 100 ml. After thoroughly mixing, the solution was transferred to a closed-pressure reservoir pipet and 10-ml. portions were delivered into ampoules. The ampoules were capped at once with gelatin capsules and placed in an ice-bath. The ampoules were sealed with a hand-torch while still in the ice-bath.

Ampoules 2 and 9 were titrated immediately. The remaining ampoules were placed in the constant temperature bath in between the titration of the two samples. The concentration of the ethyl acetate at the time the ampoules were placed in the constant temperature bath was calculated from the known hydrazine concentration. At fixed intervals the ampoules were broken open and the contents transferred to a beaker containing 150 ml. of water and sufficient standard acid to quench the reaction. The excess acid was then back-titrated with standard sodium hydroxide solution. The titrations were followed by the use of a Beckman model H *p*H meter, the end-points being determined by plots of ml. of base against change of *p*H.

The possibility that some hydrolysis might have occurred also was checked in every case. The hydrazonium ion concentration was always the same as the concentration of hydrazine remaining unreacted, indicating that no hydrolysis had taken place. The method used for the determination of the hydrazonium ion was based on the fact that this ion reacts with formaldehyde with the liberation of protons.[3] The increase in acidity may then be determined by titration with a standard base. This method gives excellent results. This analysis was carried out on the solution in which the unreacted hydrazine had already been determined.

The solutions to which the butyl alcohols were to be added were made up in more concentrated form, from which smaller aliquots were taken. This was necessary because of the greater volume per mole of the butyl alcohols compared with the lower alcohols. The amount of dioxane present in these solutions, therefore, was less.

With slight variations, solutions II to V were prepared in a similar way and the analytical procedures remained the same except for solutions IV and V. In the latter cases, the ampoules were opened and the contents transferred to a beaker containing 150 ml. of methanol and excess of standard acid. This change was necessary to prevent the separation of two layers.

Calculations and Results

The reaction of hydrazine with ethyl acetate follows second-order kinetics and the *k* values were calculated from the second-order rate equation

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

The values for the energies and entropies of activation were calculated, together with their errors, in the same way as reported previously.[1c] The data for the five types of solutions studied are shown in Tables I to V.

Discussion

Hydrazinolysis, similar to ammonolysis, involves a nucleophilic attack on the carbonyl carbon atom of the ester. The transfer of a proton is

TABLE I

SPECIFIC AND RELATIVE REACTION VELOCITY CONSTANTS AT 50% ETHYL ACETATE REACTED AT 30° (UNITS, LITERS MOLE^{-1} SECOND^{-1})

Solution I, 2.5 *M* water, 1 *M* ethyl acetate, 5 *M* ethyl alcohol, 5 *M* alcohol, 2 *M* hydrazine and dioxane

Alcohol	Concn., moles	$k \times 10^5$	Rel. rate constants
Methyl	5	1.042 ± 0.083	1.45
Ethyl	5	1.167 ± .028	1.62
n-Propyl	5	1.314 ± .042	1.83
i-Propyl	5	1.008 ± .014	1.40
n-Butyl	5	2.861 ± .083	3.99
i-Butyl	5	2.291 ± .111	3.19
s-Butyl	5	1.639 ± .014	2.28
t-Butyl	5	1.236 ± .028	1.72
Propylene glycol	2.5[a]	1.453 ± .028	2.02
Ethylene glycol	2.5[a]	1.694 ± .119	2.36
No added alcohol	0	0.717 ± .028	1.00

[a] Molar concentrations reduced to keep actual hydroxyl concentration constant.

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(2) The solution containing 13.5 moles of ethyl alcohol had no dioxane as diluent.

(3) B. Stempel, *Z. anal. Chem.*, **91**, 413 (1933).

TABLE II

VELOCITY CONSTANTS[a] AT 50% ETHYL ACETATE REACTED

Solution II, 2.5 *M* water, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and dioxane

Alcohol	$k \times 10^5$		
	20°	30°	40°
Methyl	0.589 ± 0.008	0.869 ± 0.042	1.197 ± 0.017
Ethyl	.489 ± .003	.717 ± .014	0.966 ± .006
n-Propyl	.650 ± .003	.924 ± .006	1.225 ± .010
i-Propyl	.604 ± .006	.781 ± .003	1.111 ± .006
n-Butyl	1.058 ± .006	1.517 ± .003	1.917 ± .014
i-Butyl	0.792 ± .014	1.139 ± .014	1.469 ± .017
s-Butyl	.633 ± .001	0.903 ± .014	1.153 ± .006
t-Butyl	.486 ± .003	.644 ± .011	0.867 ± .017

[a] *k* is in liters mole^{-1} second^{-1}.

TABLE III

ENERGIES AND ENTROPIES OF ACTIVATION AT 50% ETHYL ACETATE REACTED

Solution II, 2.5 *M* water, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and dioxane

Alcohol	*E*a, cal.	$-\Delta S^*$, e.u.
Methyl	6456 ± 553	62.45 ± 1.29
Ethyl	6200 ± 194	63.68 ± 0.33
n-Propyl	5762 ± 99	64.62 ± .23
i-Propyl	5576 ± 103	65.45 ± .26
n-Butyl	5391 ± 158	64.89 ± .37
i-Butyl	5619 ± 215	64.70 ± .50
s-Butyl	5436 ± 169	65.77 ± .39
t-Butyl	5276 ± 249	66.85 ± .58

TABLE IV

VELOCITY CONSTANTS[a] AT 50% ETHYL ACETATE REACTED AT 30°

Solution III, 2.5 *M* water, 1 *M* ethyl acetate, 5–13.5 *M* ethyl alcohol,[b] 2 *M* hydrazine and dioxane

Ethyl alcohol, *M*	$k \times 10^5$
5	0.717 ± 0.028
10	1.167 ± .028
11.5	1.856 ± .056
12.5	2.611 ± .111
13.5	3.514 ± .119

[a] Units, liters mole^{-1} second^{-1}. [b] The solution having 13.5 moles of ethyl alcohol contained no dioxane as diluent.

TABLE V

VELOCITY CONSTANTS[a] AT 50% ETHYL ACETATE REACTED AT 30°

Solution IV, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and benzene

Alcohol (5 *M*)	$k \times 10^5$	Rel. rate constants
Methyl	1.064 ± 0.028	1.43
Ethyl	0.750 ± .014	1.01
n-Propyl	0.742 ± .014	1.00
n-Butyl	1.272 ± .028	1.71

VELOCITY CONSTANTS[a] AT 50% ETHYL ACETATE REACTED AT 30°

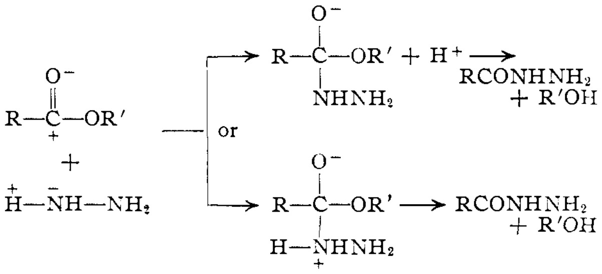
Solution V, 1 *M* ethyl acetate, 5 *M* alcohol, 2 *M* hydrazine and cyclohexane

Alcohol (5 *M*)	$k \times 10^5$
Ethyl	4.08 ± 0.035
n-Propyl	3.36 ± .014
n-Butyl	3.50 ± .056

[a] Units, liters mole^{-1} second^{-1}.

involved in both cases but it is not known at what point this transfer takes place.

As in the case of the ammonolysis of esters, the presence of hydroxylated solvents facilitates the hydrazinolysis of esters. In the present study the effects of the monohydric alcohols, from methyl alcohol through the four butyl alcohols, on the rate of hydrazinolysis have been examined (Tables I and II). The primary alcohols have the greatest effect and *n*-butyl alcohol, the best of the monohydric alcohols, is even better than ethylene glycol in promoting the reaction.



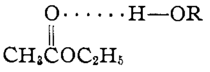
It should be noted that the total amount of alcohol present in solution I is twice as great as the total amount in solution II. Consequently the *k* values in Table I are greater than those in Table II, but the relative position of any given alcohol in the series remains the same. The data shown in Table I were obtained from the initial experiments using solution I. The solvent system was then simplified to some extent by leaving out the ethyl alcohol but retaining the 5 *M* concentration of the other alcohol (solution II). The data from the study of the latter solution are shown in Table II.

The data in this table, as well as in Table I, are not entirely comparable except in the case of the four isomeric butyl alcohols. The concentration of dioxane decreases as the molecular weight of the alcohol increases. As a result, the solutions containing the butyl alcohols had present relatively small amounts of dioxane. That dioxane does exert a small retarding effect on the reaction rate will be shown later. The data from the four butyl alcohols, however, are comparable since their solutions contained practically the same amount of dioxane. The activation energies for the entire series decrease irregularly with increase in molecular weight of the alcohols, while the entropy values increase with increase in molecular weight of the alcohols (Table III).

The data reported in Table IV were obtained to determine the effect of increasing ethyl alcohol concentration on the reaction rates. From 11.5 to 13.5 moles there appears to be a linear increase in rate constant. Below 11.5 moles the increase is not linear, suggesting that the dioxane does affect the reaction rate.

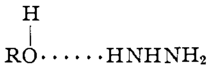
Finally, the hydrazinolysis reaction was run in solutions containing no water or dioxane. In solution IV, benzene was used as the diluent, and in solution V, cyclohexane was used as the diluent. The results are included in Table V. Where benzene is used as the diluent, it will be noted that *n*-butyl alcohol still exerts the greatest promoting effect on the reaction rate, although methyl alcohol shows an increased effect on the reaction rate in this system. Ethylene glycol was not compatible with this system and could not be evaluated. It will be noted that where cyclohexane was used as diluent the reaction rates are higher and *n*-butyl alcohol is no longer the most effective alcohol in promoting hydrazinolysis. Unfortunately neither methyl alcohol nor ethylene glycol was soluble in this system and could not be evaluated.

Considerably more work will be necessary before the solvent effects noted in the present investigation can be explained adequately. The differences noted cannot be explained on the basis of the differences in dielectric constant alone, for if this were the case *n*-butyl alcohol should be less effective than methyl alcohol (Tables I and II). Certain conclusions from the present data appear to be warranted. It may be safely assumed that in solution V the cyclohexane is relatively inert to the other molecules present. Consequently the hydrazine, ester and alcohol are more free to form hydrogen-bonded intermediates of the types



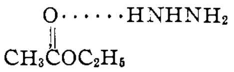
$$\overset{O\cdots\cdots H-OR}{\overset{\|}{CH_3COC_2H_5}}$$

A



$$\overset{H}{\overset{|}{RO}}\cdots\cdots HNHNH_2$$

B

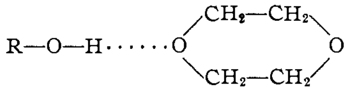


$$\overset{O\cdots\cdots HNHNH_2}{\overset{\|}{CH_3COC_2H_5}}$$

C

These are the types that would be expected to promote hydrazinolysis. The contribution of A should be dependent on the acidity of the alcohol, while the effect of B should be related to the basicity of the alcohol. That C does not play a major role is indicated by the fact that both ammonolysis and hydrazinolysis of esters proceed more slowly in the absence of hydroxylated solvents. In benzene and cyclohexane solutions, type A is predominant with the more acidic methyl and ethyl alcohols. The fact that *n*-butyl alcohol is more effective than *n*-propyl alcohol suggests that the type B hydrogen-bonded intermediate is more effective in this case. The somewhat slower rates obtained in benzene may be accounted for by assuming the formation of complexes between the benzene molecules and the solute molecules. The slower rates thus would be the result of a competing process plus any steric factors that are involved.

The slower rates obtained for solutions I and II may be interpreted in a similar way. These systems are too complex to permit many conclusions. A greater number of hydrogen-bonded intermediates are possible and that some of them retard the reactions is indicated by the slower rates obtained. If one considers only the normal alcohols in these two series, the rates would appear to be dependent on their relative basicities. It must be remembered, however, that there is a decreasing amount of dioxane present in going from CH_3OH to C_4H_9OH. Hydrogen-bonded intermediates of the type



D

could well account for the results. The extent of formation of D would depend on the relative acidity of the alcohol and the amount of dioxane present. Type D would not be expected to promote hydrazinolysis.

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS AND CHEMISTRY, GAKUSXHIN UNIVERSITY]

On the Thermal Dissociation of Organic Compounds. XI. The Effects of the Substituents on the Thermal Dissociation of Urethans in Amine Solvent

BY TERUAKI MUKAIYAMA AND MASARU IWANAMI

RECEIVED JUNE 12, 1956

Urethans dissociate by the double transfer of their proton in the presence of bases. The rate constants, the activation energies and the entropies of activation of the thermal dissociation of various *ortho*, *meta* and *para* substituted N-phenylbenzyl carbamates in amine solvent were measured throughout temperature interval 130 ~ 170°. Linear relationships between the activation energies and the entropies of activation for *meta* and *para* derivatives and *ortho* derivatives, respectively, were found.

Introduction

Previous reports in this series[1,2] have shown that on heating, ureas and urethans dissociate into their components in the presence of either fatty acids or amines.

$$RNHCONHR \rightleftarrows R-N=C=O + H_2NR \quad (1)$$

$$RHNCOOR \rightleftarrows R-N=C=O + HO-R \quad (2)$$

The kinetics of the thermal dissociation of urethans in amine solvents[2] has been studied and the mechanism shown in equations 2 and 3 has been proposed. As isocyanates add to amines instantaneously to form ureas quantitatively, reaction 2

$$R-N=C=O + H_2NR \rightleftarrows RHNCONHR \quad (3)$$

is the rate-determining step in the above sequence. Therefore, when urethan is allowed to react in a large excess of amine, the rate constants for the dissociation of urethan become measurable by determining the amount of remaining amine.

In the present investigation, the rate constants, the activation energies and the entropies of activation of the dissociation of N-phenyl-benzyl carbamates substituted with methyl, methoxy, chloro and nitro groups in the *ortho*, *meta* and *para* positions were determined to clarify the effect of sub-

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[1] T. Mukaiyama, S. Ozaki and Y. Kobayashi, *Bull. Chem. Soc. Japan*, **29**, 51 (1956).

[2] T. Mukaiyama and Y. Hoshino, THIS JOURNAL **78**, 1946 (1956).