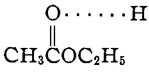
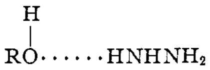
diluent the reaction rates are higher and *n*-butyl alcohol is no longer the most effective alcohol in promoting hydrazinolysis. Unfortunately neither methyl alcohol nor ethylene glycol was soluble in this system and could not be evaluated.

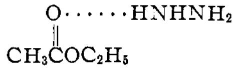
Considerably more work will be necessary before the solvent effects noted in the present investigation can be explained adequately. The differences noted cannot be explained on the basis of the differences in dielectric constant alone, for if this were the case *n*-butyl alcohol should be less effective 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


$CH_3C(=O\cdots\cdots H{-}OR)OC_2H_5$

A


$RO(H)\cdots\cdots HNHNH_2$

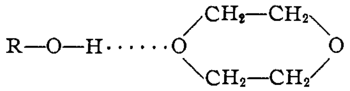
B


$CH_3C(=O\cdots\cdots HNHNH_2)OC_2H_5$

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.

$$RNHCONHR \rightleftharpoons R{-}N{=}C{=}O + H_2NR \quad (1)$$

$$RHNCOOR \rightleftharpoons R{-}N{=}C{=}O + HO{-}R \quad (2)$$

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

$$R{-}N{=}C{=}O + H_2NR \rightleftharpoons RHNCONHR \quad (3)$$

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).

stituents on the dissociation of urethans in amine solvents.

The results show that *meta* and *para* substituted urethans approximately follow the Hammett equation with a ρ-value of 0.538, that is, the rates of dissociation of urethans are accelerated by introducing electron-attracting groups. *ortho*-Substituted urethans dissociate faster than the corresponding *meta* and *para* substituted urethans; this may be attributed to steric effects.

It can be concluded that, in amine solvents, the process of deprotonation of urethan by the solvent may be a predominant factor for the dissociation.

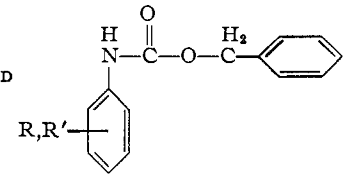
Experimental

Procedure.—The experimental procedure was essentially that used in the earlier investigation.[2] The amount of amine remaining was determined by titrating with 0.025 *N* hydrochloric acid, using methyl red as indicator.

Materials.—N-Phenyl-benzyl carbamates were prepared from benzyl chlorocarbonate and the corresponding amines according to the procedure of Bergmann and Zervas.[3] Benzyl alcohol and ethanolamine were purified by vacuum distillation. The boiling points for these substances were 114° at 38 mm. and 74° at 12 mm., respectively.

TABLE I

MELTING POINTS AND ANALYSES FOR



R	R′	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	78 (77)[a]		
o-Methyl	H	82.5 ~ 83.5 (83.5)[a]		
o-Methyl	*m*-Nitro	150 ~ 151	9.79	10.12
m-Methyl	H	54[d]	5.80	6.12
p-Methyl	H	82.5 ~ 83 (83)[a]		
m-Methoxy	H	72	5.44	5.77
p-Methoxy	H	98.5 ~ 99 (98)[a]		
o-Chloro	H	55 ~ 55.5	5.35	5.56
m-Chloro	H	45 ~ 46	5.35	5.58
p-Chloro	H	110	5.35	5.56
o-Nitro	H	61 ~ 62	10.29	10.04
o-Nitro	*p*-Methyl	97.5 ~ 98	9.79	10.05
m-Nitro	H	115.5 ~ 116 (116 ~ 117)[b]		
p-Nitro	H	155 (157)[c]		

[a] N. C. Bergstrom and A. E. Martell, THIS JOURNAL, **67**, 494 (1945). [b] C. Naegli and A. Tyabji, *Helv. Chim. Acta*, **18**, 142 (1935). [c] V. Hoogstraten, *Rec. trav. chim.*, **51**, 426 (1932). [d] P. Ruggli and H. Dahn (*Helv. Chim. Acta*, **27**, 1116 (1944)) obtained this substance as an oily product, however, it can be recrystallized from ligroin, m.p. 54°.

The rate constants of the thermal dissociation of urethans (1 mole) in ethanolamine (10 moles) and benzyl alcohol (50 moles) were determined. On plotting the logarithm of the amount of amine, ΔY, remaining in the reaction *vs.* time, we have obtained a straight line, indicating a first-order reaction. The rate constants are given by the gradient of such a plot,[4] as shown in Fig. 1.

Results and Discussion

The effect of substituents on the rate of thermal dissociation of urethans nearly follows the Hammett equation (Fig. 2). The plot of the logarithm of the rate constants *vs.* reciprocal absolute temperature gave satisfactory straight lines from which activation energies and entropies of activation were obtained (Table II).

Figure 3 presents the linear relationship between activation energies and entropies of activation. The results show a definite increase in the entropies of activation with increasing activation energies and parallelism between the *ortho* series and the *meta* and *para* series.

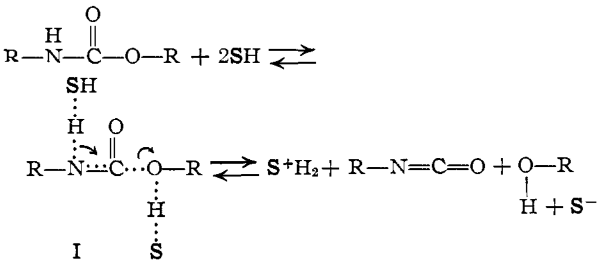
The results of the rate measurements given in Table II show that for substitution in the *meta* and *para* position, the greater the electron-attracting power of the substituent the greater is the rate constant and the lower the activation energy; the greater the electron-donating power of the substituent the lower the rate constant and the greater the activation energy. As shown in Fig. 2, log *k* is approximately a linear function of the substituent constants[5] given by Hammett and the gradient of the plot gave a value for the reaction constant, ρ, of $+0.538$.

In *meta* and *para* substituted urethans, the hydrogen atom attached to nitrogen is labilized by electron-attracting substituents, and the formation of the conjugate base in basic media is a predominant factor in the dissociation. The dissociation proceeds by eliminating alcohol from this conjugate base.

ortho Substituents, in contrast to *meta* and *para* substituents, accelerate the dissociation regardless of their nature and changes in both activation energy and entropy of activation are found. The results can be attributed to the steric effect of the *ortho* substituents, which facilitates the deprotonation of the urethan linkage, and dissociation of urethan.

It will be noted (Fig. 3) that the activation energy is approximately a linear function of the entropy of activation for *meta* and *para* substituted urethans and *ortho* substituted urethans, respectively. For *meta* and *para* derivatives, electron-attracting substituents give lower activation energy and a more negative entropy. For *ortho* derivatives, a combined decrease in both the activation energy and the entropy of activation which may be attributed to the steric requirement of the *ortho* substituents is found.

As mentioned in the previous report, urethan is amphoteric toward solvent molecules: it can dissociate by double transfer of a proton in the presence of either acidic or basic solvents. The termolecular mechanism for the dissociation of urethan is[2]



where SH represents solvent.

In the transition state I, one solvent acts as a base to accept a proton and the other acts as an acid to donate a proton at the same time. By the shift of an electron pair, the state I dissociates.

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(3) M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

(4) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 188.

TABLE II

THE RATE CONSTANTS AND THE THERMODYNAMIC QUANTITIES FOR THE THERMAL DISSOCIATION OF URETHANS IN ETHANOLAMINE AT 150°

R	R′	$k \times 10^{-4}$, sec.$^{-1}$ 130 (t, °C.)	140	150	155	160	170	E, kcal.	$\Delta S^{\ddagger}$, e.u.
o-Nitro	H	2.33	3.67	5.63	6.80	8.45	12.30	15.5	−37.4
o-Methyl	*m*-Nitro	1.93	3.10	4.80	5.57	7.30	10.95	16.0	−36.5
o-Methyl	H	1.65	2.67	4.41	5.20	6.94	10.40	16.4	−35.8
o-Nitro	*p*-Methyl	1.34	2.37	3.81	4.60	5.80	9.00	16.9	−34.8
o-Chloro	H	1.28	2.16	3.53	4.33	5.53	8.61	17.3	−34.1
p-Nitro	H	1.15	2.12	3.81	4.56	6.07	11.50	19.7	−28.1
m-Chloro	H	1.00	1.83	3.57	4.13	5.73	9.37	20.0	−27.8
m-Nitro	H	0.996	1.75	3.10	4.06	5.53	9.12	20.3	−27.2
p-Chloro	H	.749	1.32	2.51	3.13	4.33	7.33	20.8	−26.5
m-Methoxy	H	.584	1.20	2.13	2.67	3.66	6.35	21.1	−26.0
H	H	.550	1.03	1.97	2.44	3.40	5.77	21.4	−25.6
m-Methyl	H	.453	0.891	1.75	2.23	3.16	5.38	22.4	−23.6
p-Methyl	H	.270	.596	1.18	1.50	2.10	3.93	24.1	−20.4
p-Methoxy	H	.241	.496	1.06	1.33	1.90	3.63	24.4	−19.7

In order to interpret the experimental results on the dissociation mechanism, it is necessary to assume that solvent interaction which assists in the proton transfer of urethan at the transition state is affected by the substituents.

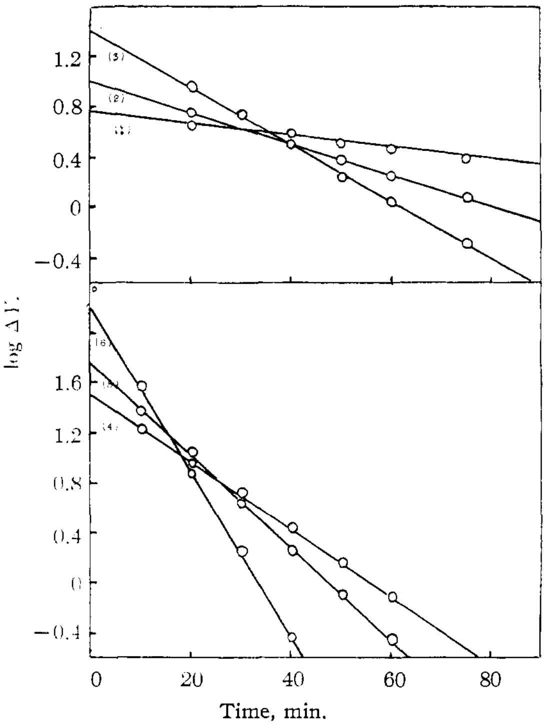


Fig. 1.—Thermal dissociation of N-*p*-nitrophenyl-benzyl carbamate in ethanolamine; the plot of log ΔY against t: 1, 130.0°; 2, 140.0°; 3, 150.0°; 4, 155.0°; 5, 160.0°; 6, 170.0°.

The urethan linkage with electron-attracting substituents is partially positively charged in the ground state and donation of a proton to basic solvents is facilitated. When proton transfer begins, the bond electrons of the weakened nitrogen-hydrogen bond migrate in the direction of the carbonyl group and the protonic solvent, such as solvent alcohol, is attracted more to the negative end of urethan. Therefore urethans with electron-attracting substituents donate a proton easily;

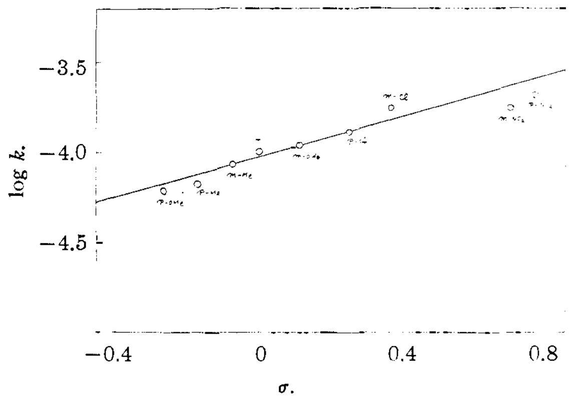


Fig. 2.—Plot of log k vs. the Hammett σ-values.[5]

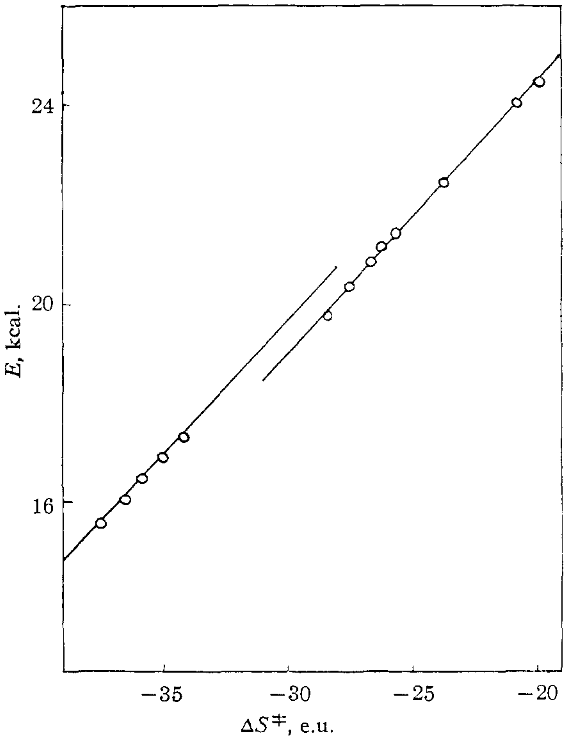
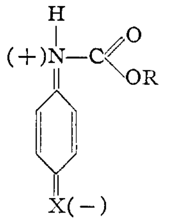
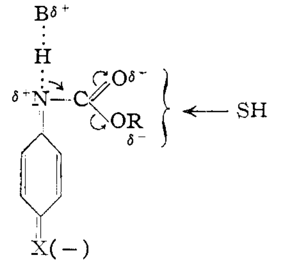


Fig. 3.—Linear relation between energies and entropies of activation for the thermal dissociation of urethans.

however, they solvate more with the transition state and less with the ground state. Consequently the lower activation energy and greater negative entropy of activation in the activation process is expected.


ground state


transition state

A similar argument suggests that urethans with electron-donating substituents are slow to donate a proton; however, they solvate more with the ground state and solvation in the transition state is not so noticeable as in the former urethans. Therefore the higher activation energy and a lower negative entropy of activation is expected.

ortho Substituted urethans give a lower activation energy and a more negative entropy of activation than those of urethans correspondingly substituted in the *meta* and *para* positions. Because of the steric strain in *ortho* derivatives, the hydrogen atom of the urethan linkage becomes more acidic, and donates a proton to a base more readily and thus lowers the activation energy. However, solvation is less with the ground state by reason of steric hindrance of the *ortho* substituents. This may explain the more negative entropy in *ortho* derivatives.

Acknowledgment.—The authors wish to express their hearty thanks to Prof. Toshio Hoshino for his encouragement throughout the course of this experiment.

MEJIRO, TOSHIMA-KU, TOKYO, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Molecular Compounds. VIII. Evidence for the Existence of 2:1 and 1:2-Complexes in Chloroform Solutions of 1,3,5-Trinitrobenzene and N,N-Dimethylaniline

BY SIDNEY D. ROSS AND MORTIMER M. LABES

RECEIVED JULY 30, 1956

It is shown that 1,3,5-trinitrobenzene and N,N-dimethylaniline form 1:2- and 2:1-complexes as well as a 1:1-complex in chloroform solution. The effects of the presence of the 1:2- and 2:1-complexes on the determination of the equilibrium constant for formation of the 1:1-complex have been explored. The equilibrium constants and extinction coefficients have been determined for the 1:1-complex and 1:2-complex.

The equilibrium constant for formation of the 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex in chloroform solution at 17.5° has been measured by Ley and Grau[1] both by a solubility method and spectroscopically. The first method gave an average value of 1.45 l. mole^{-1}; the latter method resulted in an average value of 1.82 l. mole^{-1}, and the authors considered the first of these values the more reliable one. More recent spectroscopic measurements by Foster and Hammick[2] have resulted in a value of 1.3 l. mole^{1} for the equilibrium constant at 21°.

In connection with other studies, we have recently measured this equilibrium constant at 24.8 ± 0.1° by the spectroscopic method. Our initial values were strongly at variance with all three of the previous results and led to the more detailed study which is described below.

Experimental

Solvents and Reagents.—Baker and Adamson Reagent Grade chloroform, containing 0.75% ethanol as stabilizer, was used without further purification. Eastman Kodak Co. white label aniline and N,N-dimethylaniline were distilled *in vacuo* from calcium hydride immediately before use, and the middle fractions, b.p. 65° at 8 mm. and 70° at 10 mm., respectively, were used. 1,3,5-Trinitrobenzene, Eastman Kodak Co. white label, was crystallized once from glacial acetic acid and twice from absolute ethanol; m.p. 121°. Naphthalene, Eastman Kodak Co. white label, was crystallized twice from methanol as colorless plates, m.p. 80–81°.

The 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex was prepared by pouring a hot, concentrated solution of the trinitrobenzene in ethanol into a slight excess of hot N,N-dimethylaniline. On cooling, the complex separates as dark violet needles, m.p. 105–108°, m.p. 110–111° after crystallization from ethanol.[3]

The 1:1 1,3,5-trinitrobenzene–aniline complex was prepared in the same manner. It was obtained as orange-red crystals, m.p. 124–125.5° after crystallization from ethanol.[3]

The 1:1 1,3,5-trinitrobenzene–naphthalene complex was prepared by dissolving separately equimolar amounts of the two components in minimum amounts of hot ethanol and mixing the two solutions. On cooling, the 1:1-complex separates as pale yellow needles, m.p. 153–154°.[3]

The Absorption Spectra Measurements.—Stoppered 1-cm. absorption cells were used in a Beckman model DU spectrophotometer. The cell housing was maintained at constant temperature by means of two Beckman thermospacers through which water from a constant temperature bath was circulated. A detailed description of the experimental methods used in determining the equilibrium constant has been given previously.[4]

Results and Discussion

Table I presents the results of representative measurements of the equilibrium constant for formation of the 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex in chloroform at 24.8 ± 0.1°. These measurements result from thirteen different sets of amine and trinitrobenzene concentrations, with the former varied from 0.92

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(1) H. Ley and R. Grau, *Ber.*, **58**, 1765 (1925).

(2) R. Foster and D. Ll. Hammick, *J. Chem. Soc.*, 2685 (1954).

(3) P. Hepp, *Ann.*, **215**, 358, 377 (1882).

(4) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, **76**, 69 (1954).