n-amyl, have been found to lie between 0.7 and 1.0, those of secondary propyl and butyl alcohols to be about one-third, and those of tertiary butyl and amyl alcohols to be less than one per cent. of the relative reaction velocity of methyl alcohol.

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[CONTRIBUTION NO. 107 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

Relative Velocities of Reaction of Amines with Phenyl Isocyanate

BY TENNEY L. DAVIS AND FRED EBERSOLE

The relative reaction velocities of several amines with phenyl isocyanate have been determined by a method similar to that described in the preceding paper, except that the experiments were carried out in dry ether solution at 0° and the compositions of the mixtures resulting from the reactions were ascertained by means of melting point determinations and melting point–composition diagrams.

The relatively high melting points of phenylurea and the N′-substituted phenylureas made the determination of the melting point (taken as the temperature of the first appearance of the meniscus) perfectly feasible and adequate for the determination of the composition of the mixtures resulting from the reactions. The ether solutions were evaporated rapidly at room temperature, blank experiments having shown that the phenylureas present in the solution at 0° were not affected during the evaporation at room temperature by the amines which were also present. The residues, after being powdered, were freed from last traces of amines by drying over concd. sulfuric acid and phosphorus pentoxide in a desiccator. They were then just barely fused, cooled, powdered, and again dried for the melting point determination. The results, treated in the same way as in the preceding paper, are summarized in Tables I and II.

TABLE I

RELATIVE VELOCITIES OF COMBINATION OF AMINES WITH PHENYL ISOCYANATE

Values from Single Experiments

Expt.	Amines	Observed distribution ratio	Calcd. ratio of velocity constants
a	*n*-Propyl/ammonia	81.0/19.0	7.88
b	Aniline/ammonia	41.0/59.0	0.576
c	*n*-Butyl/*n*-amyl	50.0/50.0	1.00
d	*n*-Propyl/aniline	88.0/12.0	16.6
e	Ethyl/*n*-propyl	53.0/47.0	1.19
f	Ethyl/*n*-butyl	51.2/48.8	1.07

TABLE II

RELATIVE VELOCITIES OF COMBINATION OF AMINES WITH PHENYL ISOCYANATE

Values from All Relevant Experiments

Amine	Expts.	*K*	*K* av.	Av. dev. from av.	Probable error, %
Ammonia	..	1.00	1.00		
Ethyl	ae	9.37			
	bde	10.17	9.72	0.35	3.6
n-Propyl	a	7.88			
	bd	8.56	8.22	.34	4.1
n-Butyl	aef	8.74			
	bdef	9.59	9.17	.42	4.6
n-Amyl	aefc	8.74			
	bdefc	9.59	9.17	.42	4.6
Aniline	b	0.576			
	ad	.478	0.53	.049	9.3

The relative reaction velocity of aniline with phenyl isocyanate, about half that of ammonia, and those of the aliphatic primary amines, between eight and ten times that of ammonia, accord with qualitative observations on the urea dearrangement. Phenylurea dearranges more readily than urea, the monoalkylureas distinctly less so.

The relative reaction velocities of ethyl-, *n*-propyl-, *n*-butyl- and *n*-amylamine with phenyl isocyanate, while they are of the same order of magnitude, are by no means identical. In Table III the relative reaction velocities of the amines in ether at 0° are compared with the relative

TABLE III

COMPARISON OF THE RELATIVE REACTION VELOCITIES OF ALCOHOLS AND OF AMINES WITH PHENYL ISOCYANATE

	Relative reaction velocities				
	Alcohols relative to methyl in benzene at 26°	Amines relative to ammonia in ether at 0°	Ratio	Dev. from av. ratio	% Dev.
Ethyl	0.962	9.72	0.0989	0.0008	0.8
n-Propyl	.782	8.22	.0951	.0046	4.8
n-Butyl	.972	9.17	.1059	.0062	5.9
n-Amyl	.908	9.17	.0990	.0007	0.7

reaction velocities of the corresponding primary alcohols in benzene at 26°. Other experiments, carried out in this Laboratory, indicate that the solvent is without effect upon the relative velocities of these reactions. The circumstance that the amines are compared with ammonia and the alcohols with methyl alcohol need cause no concern since it is the relative magnitude of the numbers in each series which is at issue. One series is reported at one temperature, the other series at another, but the agreement of the numbers in the third column suggests either that temperature does not affect *relative* velocities, as seems probable, or that the effect in these particular experiments is small. The constancy of the ratio of the corresponding figures of the two series is excellent, the deviations from the average being less than the probable error in the determinations of the relative reaction velocities of the amines. As far then as these four alkyl groups are concerned, their effect upon the reactivity of the primary alcohols toward phenyl isocyanate is directly proportional to their effect upon the reactivity of the primary amines toward the same reagent. It seems probable that the same law holds for other alkyl groups and for other reagents beside phenyl isocyanate.

Summary

The relative reaction velocities of a number of amines with phenyl isocyanate in dry ether at 0° have been measured.

The relative reaction velocity of aniline is about half and those of ethyl-, *n*-propyl-, *n*-butyl- and *n*-amylamine between eight and ten times that of ammonia.

The effect of the ethyl, *n*-propyl, *n*-butyl and *n*-amyl groups upon the reactivity of the primary alcohols toward phenyl isocyanate is proportional to their effect upon the reactivity of the primary amines toward the same reagent.

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[Contribution from the Illinois State Water Survey]

The Anaerobic Fermentation of Lignin

By C. S. Boruff and A. M. Buswell

In 1928, while studying the anaerobic fermentation of fibrous materials, the writers noted that the pith in materials such as cornstalks was quickly and very completely fermented under anaerobic conditions to carbon dioxide and methane.[1] From data obtained in numerous studies, it was apparent that the lignin fraction in the pith and in the general body of the cornstalks was furnishing part of the gas recovered.[2] The large amount of organic matter used to start these earlier fermentations, however, made it difficult to definitely establish this fact. Since the gasification of lignin had not been previously observed,[3–12] the work was repeated under conditions designed to give quantitative data on lignin.

Studies on Isolated Lignin

The anaerobic fermentation of lignin isolated from cornstalks by four different methods, namely Kalb, Friedrich, and the two different Phillips procedures, has been investigated. Lignin prepared by the Kalb procedure[13] when inoculated with organic matter from cultures of carbon dioxide–methane producing bacteria gave only small volumes of gas over that from the control (5 g. of lignin gave 133 cc. of methane and 43 cc. of carbon dioxide in one experiment and 368 cc. of methane and no carbon dioxide in another; both experiments were incubated at 25–30° for thirty-three days). Friedrich[14] lignin also gave small volumes of gas, namely, 140 cc. of methane and 6 cc. of carbon dioxide from 2.0 g. of lignin in thirty-three days. In these three studies no correction was made for the carbon dioxide retained in the mother liquor. This undoubtedly averaged about 1000 cc. Lignin prepared by hydrochloric acid[15] and by sodium

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