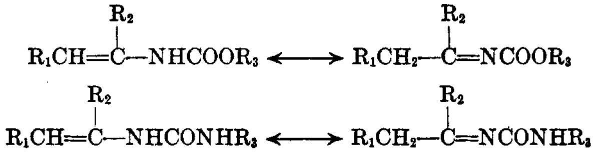
[Contribution from the Research Laboratory of Resources Utilization, Tokyo Institute of Technology]

Studies on 1-Alkenyl Isocyanates and Their Derivatives[1]

MASAO SATO

Received March 14, 1960

Various 1-alkenyl isocyanates were prepared by the reactions between the corresponding acid chlorides and sodium azide. Infrared spectra of these isocyanates and the derivatives which were obtained from the reactions of these isocyanates with alcohols and amines were determined. The isomerization reactions of alkyl *N*-1-alkenyl carbamates and *N*-1-alkenyl-*N'*-alkylureas were discussed as the following types:

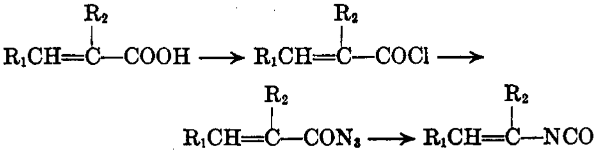


$$R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}NHCOOR_3 \longleftrightarrow R_1CH_2{-}\overset{R_2}{\overset{|}{C}}{=}NCOOR_3$$

$$R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}NHCONHR_3 \longleftrightarrow R_1CH_2{-}\overset{R_2}{\overset{|}{C}}{=}NCONHR_3$$

In this laboratory, the preparation[2–6,8] of various 1-alkenyl isocyanates, the reactions[4,5,7,8] of these isocyanates with some nucleophilic reagents—*e.g.*, amines, alcohols, and mercaptans—and the copolymerization[2,3] of vinyl isocyanate and isopropenyl isocyanate with other vinyl compounds have been studied. 1-Alkenyl isocyanates, *N*-1-alkenyl carbamates, and *N*-1-alkenylureas are very interesting materials in organic chemistry, especially in polymer chemistry, because these compounds seem to give high molecular weight substances by polymerization and copolymerization, and the polymers obtained are able to bring about further polymer reactions. But the preparation and properties of these compounds have not been investigated systematically in spite of many papers.[9–20]

Various 1-alkenyl isocyanates were prepared by following procedures:



$$R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}COOH \longrightarrow R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}COCl \longrightarrow$$

$$R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}CON_3 \longrightarrow R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}NCO$$

The physical properties and yields are collected in Table I from previous communications. As previously reported, the reactions of 1-alkenyl isocyanates with nucleophilic reagents are more complicated with saturated alkyl and aromatic isocyanates. Furthermore, the properties of *N*-1-alkenyl carbamates and *N*-1-alkenylureas are different from the usual carbamates and ureas—*e.g.*, the addition of nucleophilic reagents to a double bond, the behavior during hydrolysis to the corresponding aldehyde or ketone and carbamate or urea, and the ease of the reaction with other reagents. When the melting points of some *N*-1-alkenyl-*N'*-alkyl(or aryl) ureas were determined, it was found that the values varied with the speed of heating. In *N*-1-substituted vinyl carbamates, it was also found that the refractive indices varied with preparation conditions—*e.g.*, molar ratio of materials, the speed of distillation, the degree of vacuum, etc. On the other hand it is well known that the isomerization of α,β-alkenylamines to aldoimines or ketimines has been much described.[21–24] From these two facts, the C=C double bond seems to isomerize to the C=N double bond as follows:

---

(1) M. Sato, *J. Am. Chem. Soc.*, **82**, 3893 (1960).

(2) Y. Iwakura, M. Sato, T. Tamikado, and S. Mimashi, *Chemistry of High Polymers* (*Japan*), **13**, 125 (1956).

(3) Y. Iwakura, M. Sato, T. Tamikado, and T. Mizoguchi, Chemistry of High Polymers (Japan), **13**, 390 (1956).

(4) Y. Iwakura, M. Sato, and H. Munakata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zashi*), **79**, 148 (1958).

(5) Y. Iwakura, M. Sato, and Y. Matsuo, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zashi*), **80**, 502 (1959).

(6) Y. Iwakura, M. Sato, and A. Ikegami, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zashi*), **80**, 632 (1959).

(7) M. Sato, A. Ikegami, and Y. Iwakura, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zashi*), **80**, 635 (1959).

(8) M. Sato, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zashi*), **81**, 959 (1960).

(9) J. Hoch, *Compt. rend.*, **201**, 733 (1935).

(10) D. D. Coffman, U. S. Patent No. **2,334,476;** U.S. Patent No. **2,326,287.**

(11) G. D. Jones, U.S. Patent No. **2,514,328.**

(12) G. D. Jones, J. Zomlefer and K. Hawkins, *J. Org. Chem.*, **9**, 501 (1944).

(13) J. Hoch, *Compt. rend.*, **201**, 560 (1935).

(14) J. B. Dickey, U. S. Patent No. **2,592,252.**

(15) R. Hart, *Ind. Chem. Belg.*, **20**, 403 (1955).

(16) R. Hart, *Bull. Soc. Chem. Belg.*, **65**, 291 (1956).

(17) R. Hart and A. Dormael, *Bull. Soc. Chem. Belg.*, **65**, 571 (1956).

(18) R. Hart, *Bull. Soc. Chem. Belg.*, **66**, 229 (1957).

(19) L. Ghoses and G. Smets, *J. Polymer Sci.*, **35**, 215 (1959).

(20) G. Welzel and G. Greber, *Makromol. Chem.*, **31**, 230 (1959).

(21) M. Bredt-Savelsberg and E. Bund, *J. prak. Chem.*, **131**, 29 (1931).

(22) H. D. Zook, M. Ream, and E. W. Delchamps, *J. Am. Chem. Soc.*, **75**, 5590 (1953).

(23) W. Krabbe and K. H. Schmidt, *Ber.*, **72**, 381 (1939).

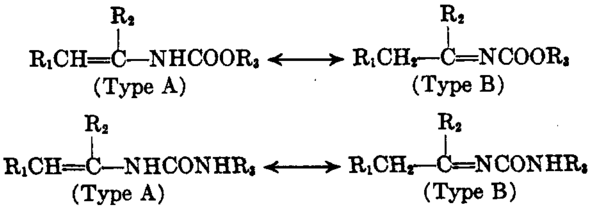
(24) W. Krabbe, A. Seher, and E. Polzin, Ber., **74**, 1892 (1941).

TABLE I

PROPERTIES AND YIELDS OF VARIOUS SUBSTITUTED ACRYLIC ACID CHLORIDES AND 1-ALKENYL ISOCYANATES

$R_1CH=C(R_2)-$		Acid Chloride			Isocyanate					
R_1	R_2	Chloride used, g.(mole)	B.p.(mm.)	Yield	NaN_3	Solvent	cc.	Yield g.(%)	B.p.(mm.)	n_D(temp.)
H	H	120(1.33)	75°(760)	73[a]	129	Anisole	400	67.2(73)	39°(760)	1.4188(20)
CH_3	H	52(0.50)	—	—[a]	48	Anisole	200	22.4(54)	81°(760)	—
C_3H_7	H	60(0.45)	65°(18)	89[b]	59	T.H.F.[c]	150	34.2(70)	133°(760)	—
C_6H_5	H	183(1.10)	150–151°(35)	83[b]	138	T.H.F.	300	71(45)	110°(18)	—
H	CH_3	104(1.0)	50–51°(138)	76[b]	98	Anisole	400	76.6(92)	61–62°(760)	1.4160(25)
H	C_2H_5	106.9(0.9)	117–119°(760)	77[a]	110	Anisole	200	78.9(90)	88°(760)	1.4242(25)
H	n-C_4H_9	97(0.66)	62°(19)	89[b]	90	T.H.F.	200	66.3(80)	66°(60)	1.4338(25)
H	n-C_6H_{13}	93(0.53)	63°(3)	91[b]	67	T.H.F.	200	69.3(85)	60°(8)	1.4408(25)
H	C_6H_{11}	49.2(0.29)	95°(14)	96[b]	50	T.H.F.	100	36.9(86)	77°(14)	1.4770(25)
H	C_6H_5	18.9(0.11)	87–88°(5)	33[b]	20	T.H.F.	60	8.2(52)	61°(5)	1.5554(25)
H	$(CH_2)_5$—NCO	38.5(0.20)	98°(5)	85[b]	40	T.H.F.	100	5.0(17)	65°(3)	1.4707(25)
H	$(CH_2)_7$—NCO	38.0(0.15)	127–129(2.5)	91[b]	65	T.H.F.	100	14.5(46)	100°(2)	1.4668(25)

[a] Reaction between the corresponding free acid and benzoyl chloride. [b] Reaction between the corresponding free acid and thionyl chloride. [c] Tetrahydrofuran.



$$R_1CH=\overset{R_2}{\overset{|}{C}}-NHCOOR_3 \longleftrightarrow R_1CH_2-\overset{R_2}{\overset{|}{C}}=NCOOR_3$$
(Type A) (Type B)

$$R_1CH=\overset{R_2}{\overset{|}{C}}-NHCONHR_4 \longleftrightarrow R_1CH_2-\overset{R_2}{\overset{|}{C}}=NCONHR_4$$
(Type A) (Type B)

In order to explain the relationship between the infrared spectra of the saturated compounds and α,β-double bond containing compounds, and the presence of the isomerization expected above, the infrared spectra of N-1-alkenyl carbamates and N-1-alkenylureas were very extensively measured.

N-1-Nonsubstituted vinyl carbamates did not isomerize, but N-1-substituted vinyl carbamates isomerized to the C═N double bond containing compounds and by means of distillation or heating, they changed into a mixture of both types. N-1-Nonsubstituted vinylureas were presumed to isomerize to a mixture of the C═C and C═N double bond containing compounds, and N-1-substituted vinylureas were found to isomerize very easily into ketimine type compounds; after heating at 40–50° or standing for a long time, they were present in a nearly pure state of type B.

EXPERIMENTAL

The infrared spectra were obtained with Perkin Elmer Model 21 and 112 spectrophotometers. A calcium fluoride, sodium chloride, and lithium fluoride prism were employed in the appropriate spectral region. Samples were obtained as follows: *1-Alkenyl isocyanates* were prepared from the reaction of the corresponding acid chlorides with sodium azide and redistilled before use (see Table I). The C═C absorption band in the 1600–1700 cm.$^{-1}$ region was studied in a 3% isocyanate–carbon tetrachloride solution (cell-thickness 0.1 mm.) with a calcium fluoride prism, while the NCO absorption band in the 2200–2300 cm.$^{-1}$ region was measured in a 0.3–0.5% isocyanate–carbon tetrachloride solution (cell-thickness 0.1 mm.) with a lithium fluoride prism. *N-1-Alkenyl carbamates* were prepared from the reaction[7] of the corresponding 1-alkenyl isocyanates with n-butyl alcohol and distilled under reduced pressure, except N-β-phenylvinyl carbamate, the N-vinyl carbamate-n-butylamine addition compound. The infrared spectra of these compounds were measured in solution or as a liquid. The solutions were prepared as a 10% (5% in some cases) solution in carbon tetrachloride and carbon disulfide, and the spectra were measured with a 0.1-mm. cell and a sodium chloride prism. In measuring in the liquid state, the spectra were obtained with a 0.01-mm. cell and a sodium chloride prism. *N-Carboethoxydiethylketimine* and *N-carboethoxymethylphenylketimine* were prepared by the reaction[13] of the corresponding ketone diethylals with ethyl carbamate and these spectra were obtained in the liquid state with a 0.01-mm. cell and a sodium chloride prism. In butyl N-isopropenyl carbamate and butyl N-1-ethylvinyl carbamate, the changes of the spectrum after varied treatment—e.g., distillation, heating at 200°, and heating with n-butyl alcohol at 100°—were measured in a 10% carbon tetrachloride solution with a calcium fluoride prism. *N-1-Alkenyl-N′-butylureas* and *N-1-alkenyl-N′-di-n-butylureas* were prepared from the reaction of a little excess of the corresponding 1-alkenyl isocyanates with n-butylamine and di-n-butylamine in absolute ether (or petroleum ether). When the product was obtained crystalline, it was dissolved in a suitable solvent at room temperature and re-

TABLE II

INFRARED SPECTRA OF VARIOUS 1-ALKENYL ISOCYANATES

$R_1CH{=}\overset{R_2}{\overset{\vert}{C}}{-}NCO$			
R_1	R_2	C=C	NCO
H	H	1629 cm.$^{-1}$	2256 cm.$^{-1}$ (and 2301 cm.$^{-1}$)
CH_3	H	1660	2265
C_3H_7	H	1665	2262
C_6H_5	H	1646	2258
H	CH_3	1651	2262
H	C_2H_5	1643	2264
H	n-C_4H_9	1645	2266
H	n-C_6H_{13}	1645	2266
H	C_6H_{11}	1639	2275 (and 2254 cm.$^{-1}$)
H	$(CH_2)_3$—NCO	1647	2263
H	$(CH_2)_7$—NCO	1645	2266

crystallized by cooling in a Dry Ice–acetone mixture. When the product was a liquid, a viscous material or a liquid-solid mixture, the spectrum was measured after the solvent and the excess reactant had been completely driven out under reduced pressure (2–3 mm.) at 50°. All of the spectra of the carbamates and ureas were measured as rapidly as possible after the compounds had been prepared. Nitrogen analysis of all the compounds showed good agreement.

RESULTS AND DISCUSSION

1-Alkenyl isocyanates. Various 1-alkenyl isocyanates prepared are shown in Table I.

The C=C and NCO stretching absorption bands of various 1-alkenyl isocyanates are given in Table II.

The positions of the C=C and C=N bands in these isocyanates do not vary greatly with those in usual alkenes[25] and isocyanates,[26,27] but the C=C band increases greatly in intensity. For α-methylenepolymethylene diisocyanates in which one NCO group is conjugated to the C=C double bond and another is not, only one band could be observed in the corresponding region.

1-Alkenyl carbamates. All of butyl *N*-1-alkenyl carbamates examined have a NH stretching absorption band which shows that these compounds consist of a pure compound of type A, or a mixture of type A and type B. Butyl *N*-ethyl carbamate has an amide band I at 1720 cm.$^{-1}$ due to the CO of the carbamate group and an amide band II at 1498 cm.$^{-1}$ which arises from the NH deformation of the carbamate group. Both bands are in the same position described in the literature[25,28] and are very intense. In *N*-1-alkenyl carbamates another band should arise from the C=C or C=N bond among an amide band I and II. *N*-1-Nonsubstituted alkenyl carbamates—*e.g.*, butyl *N*-vinyl carbamate, *N*-propenyl carbamate, and butyl *N*-β-propylpropylvinyl carbamate—have a band at 1648 cm.$^{-1}$, 1683 cm.$^{-1}$, and 1679 cm.$^{-1}$, respectively; this band arises from the C=C double bond, because the melting points, the refractive indices, the position of this band and the intensity of the NH stretching band did not vary before and after distillation. In butyl *N*-propenyl carbamate, the Lambert-Beer's law was applicable to the NH stretching band up to 0.05*M*. The intensities before and after distillation were the same, the molar absorption coefficient was 124 mole^{-1} l. cm.$^{-1}$, and its melting point and refractive index were constant. With *N,N'*-azobisisobutyronitrile as an initiator, butyl *N*-vinyl carbamate gave a glassy hard polymer. Therefore, it is evident that these *N*-1-alkenyl carbamates are difficult to isomerize into the aldimine type B, and polymerize or decompose during heating.

N-1-Substituted 1-alkenyl carbamates—*e.g.*, butyl *N*-isopropenyl carbamate, butyl *N*-1-ethylvinyl carbamate, butyl *N*-1-butylvinyl carbamate, and butyl *N*-1-cyclohexylvinyl carbamate—had two bands between the two amide bands I and II, *i.e.*, at 1654 cm.$^{-1}$ and 1681 cm.,^{1} 1652 cm.$^{-1}$ and 1685 cm.$^{-1}$, 1653 cm.$^{-1}$ and 1674 cm.,$^{-1}$ 1648 cm.$^{-1}$ and 1673 cm.,$^{-1}$ respectively. But it is not possible to assign one of the two bands to the C=C stretching band and the other to the C=N stretching band, because the C=C and C=N stretching bands are generally found in the same region. Therefore, in *N*-1-ethylvinyl carbamate the changes of the two bands during varied treatment were investigated and the results obtained are shown in Fig. 1. Curve I was obtained for the sample in which solvent and excess reagents were driven off at room temperature *in vacuo* from a reaction mixture in which both reagents were mixed at −70 to −60°and the temperature allowed to rise to room temperature. It had only a band at 1652 cm.$^{-1}$ Curve II of the sample after distillation at 72°/0.4 mm. gave a band at 1682 cm.$^{-1}$ in addition to the former. In the spectrum (curve III) of the material which was distilled after heating in a glass tube at 200° (eight hours) with an inhibitor, the intensity of the band at 1652 cm.$^{-1}$ decreased to show a shoulder, and

---

(25) L. J. Bellamy, *The Infra red Spectra of Complex Molecules*, Methuen & Co., London, 1958.

(26) H. Hoyer, *Ber.*, **89**, 2677 (1956).

(27) W. H. T. Davison, *J. Chem. Soc.*, 3712 (1953).

(28) F. Pristera. *Anal. Chem.*, **25**, 849 (1953).

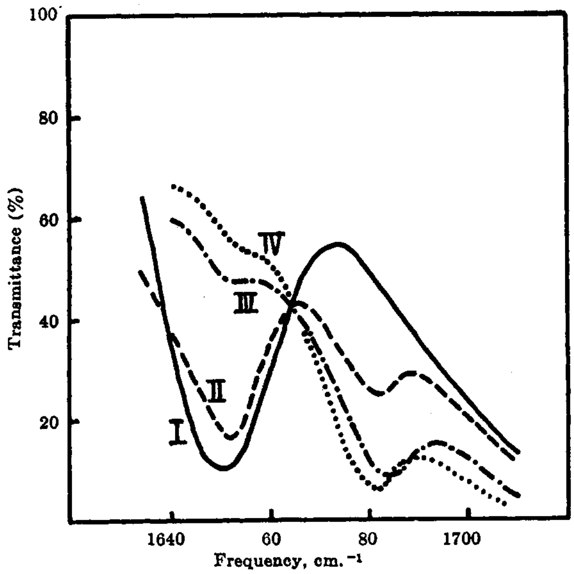


Fig. 1. Changes of infrared spectrum of N-1-ethylvinyl carbamate in 10% carbon tetrachloride solution with a calcium fluoride prism

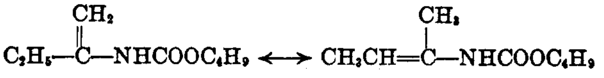
I, before distillation

II, distilled at 70°/2 mm., n_d^{20} 1.4577

III, heated at 200° (8 hr.) and distilled, n_d^{20} 1.4532

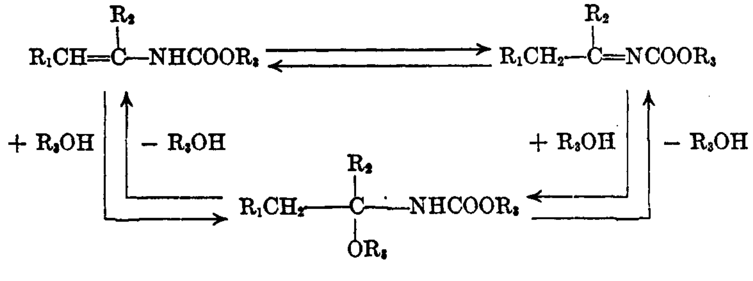
IV, heated with n-butyl alcohol at 100° (10 hr.) and distilled, n_d^{20} 1.4430

the intensity of the band at 1682 cm.$^{-1}$ increased after the treatment. When the sample of curve II was heated with n-butyl alcohol at 100° and then distilled at 2–3 mm., the intensity of the former band changed more remarkably than the sample heated at 200°, with increasing intensity at 1682 cm.$^{-1}$ These facts show that the former band arises from the C=C bond of type A, but the latter band should not be able to arise from the C=N bond, because the C=C bond in N-1-alkenyl carbamates which do not have a substituent at the α-position but do at the β-position also give rise to an absorption band in the same region—*e.g.*, butyl N-propenyl carbamate at 1683 cm.$^{-1}$ and butyl N-β-propylvinyl carbamate at 1679 cm.$^{-1}$ Therefore, it is possible to think that type A isomerizes as follows:



$$C_2H_5-\overset{\overset{\displaystyle CH_2}{\|}}{C}-NHCOOC_4H_9 \longleftrightarrow CH_3CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-NHCOOC_4H_9$$

In butyl N-isopropenyl carbamate similar results were obtained. In this case it is impossible to assign the band at 1681 cm.$^{-1}$ to the stretching vibration of the C=C bond and it can be deduced that this band would arise from the C=N bond. In the two carbamates mentioned above, the intensity of the C=C stretching band decreased qualitatively in proportion to the increase of the C=N stretching band. In butyl N-isopropenyl carbamate the Lambert-Beer's law was also applicable to the NH stretching band and the molar absorption coefficient was 116 mole^{-1} l.cm.$^{-1}$ The intensity of that band did not vary before and after distillation *in vacuo*, but the refractive index varied to some extent. It is evident from this fact that the degree of the isomerization reaction is small during distillation. N-Isopropenyl carbamate obtained from the reaction of excess n-butyl alcohol had a slightly greater molar absorption coefficient than that of the product obtained in excess isocyanate, and this fact is valuable for preparation of the pure compound. On the other hand, after heating at 100° with n-butyl alcohol for ten hours the intensity was remarkably decreased and the content of type A calculated from the intensity of the NH stretching band was *ca.* 54%. This fact may be explained as follows: When N-1-alkenyl carbamates are heated with alcohols, addition reactions occur and the products obtained from N-1-nonsubstituted vinyl carbamates are quite stable to distillation *in vacuo* without decomposition, but those obtained from N-1-substituted vinyl carbamates decompose to a mixture of type A and B owing to the unstability. For example, the following reactions occur:



$$R_1CH=\overset{\overset{\displaystyle R_2}{|}}{C}-NHCOOR_3 \rightleftarrows R_1CH_2-\overset{\overset{\displaystyle R_2}{|}}{C}=NCOOR_3$$

$$\xrightarrow{+R_3OH} R_1CH_2-\underset{\underset{\displaystyle OR_3}{|}}{\overset{\overset{\displaystyle R_2}{|}}{C}}-NHCOOR_3 \xrightarrow{-R_3OH}$$

In N-1-substituted vinyl carbamates, it is concluded that during distillation *in vacuo* or heating at 100–200°, the isomerization reaction takes place to some extent and during heating with alcohols this reaction takes place extensively, and therefore, type A of N-1-substituted vinyl carbamates is more unstable than that of N-1-nonsubstituted vinyl carbamates.

The addition reactions of nucleophilic reagents with N-1-alkenyl carbamates proceed to a different extent with various reagents—*e.g.*, alcohols, mercaptans and phenols. The addition of alcohols to N-1-alkenyl carbamates is much slower than the reaction of the corresponding 1-alkenyl isocyanates with alcohols; the rate of the reactions of isocyanates with alcohols was determined by third-order kinetics proposed by this author[1] and the term con-

TABLE III. INFRARED SPECTRA OF $R_1NHCOOC_4H_9$, CM.$^{-1}$

R_1																				
CH_3-CH_2-	3450 w	3340 w			2940 s	1720 s					1498 s		1464 s		1406 m	1378 m		1328 m		
$CH_2=CH-$	3410 w	3290 m			2908 s	1716 s		1648 s			1495 s				1399 s	1380 m		1335 m		
$CH_3-CH=CH-$		3320 m			2961 m	1705–1680 s.b		1683^b m			1526 s		1456 m		1412 w	1381 w	1358 w	1326 m		
$C_3H_7-CH=CH-$		3320 m			2962 m	1700–1678 s.b		1679^b m			1528 s		1467 m		1410 w	1380 w		1336 m		
$C_6H_5-CH=CH-$	3440 w	3320 w	3075 w	3036 w	2964 m	1710 s		1658 s	1602 w	1580 w	1513 s	1494 s			1407 m			1332 m	1331 s	
$CH_2=C(CH_3)-$	3410 w	3312 w			2890 s	1710 s	1681 sh	1654 w			1512 s		1447 s			1374 m		1325 m		
$CH_2=C(C_2H_5)-$	3420 w	3315 w			2891 s	1739 s	1685 sh	1652 sh			1512 s		1465 s			1381 m		1334 m		
$CH_2=C(C_4H_9)-$	3410 w	3312 w			2892 s	1723 s	1674 sh	1653 sh			1494 s		1458 sh			1381 m		1336 m		
$CH_2=C(C_6H_{13})-$	3400 w	3330 w			2830 s	1739 s		1650 sh			1508 s		1465 m		1413 w	1379 m		1333 m		
$CH_2=C(C_6H_{11})-$	3410 w	3312 w			2883 s	1730 s	1673 w	1648 w			1507 s		1452 w	1448 w	1395 sh	1382 m		1326 sh		
$C_4H_9OOCNH-\underset{\underset{CH_2}{\parallel}}{C}-(CH_2)_7-$	3420 w	3320 w			2930 s	1725 s	1680 sh				1508 s		1465 m			1380 w		1330 w		
$C_4H_9O-C(CH_3)_2-$	3430 w	3340 v.w			2940 s	1738 s					1500 s		1465 sh			1380 m		1336 w		
$C_4H_9NHCH(CH_3)-$	3450 w	3340 w			2950 s	1728 s					1508 s		1468 sh			1380 w		1329 w		
$C_6H_5S-CH(CH_3)-$																		1322 m		
$(C_2H_5)_2C=N-COOC_2H_5{}^a$		3320 m			2978 m	1703 s					1513 s		1462 m		1408 m	1378 m		1328 m		
$C_6H_5C(CH_3)=NCOOC_2H_5{}^a$	3435 m	3340 m	3055 m	3035 m	2976 sh	1735–1710 v.s.b		1647 s	1600 m	1578 w	1512 s	1493	1448 sh			1389 sh		1323 m	1312 sh	
CH_3-CH_2-		1236 sh	1212 s				1139 m	1117 m		1067 s		964 w	926 w	895 w	841 m	780 m	735 m			S^c
$CH_2=CH-$		1231 s	1204 s							1086 s		975 m	930 w		844 s	770 m		678 w.b		S^c
$CH_3-CH=CH-$	1295 s	1239 s				1151 w	m	1116 m		1062 m	1034 m	947 m			839 v.w.	769 w	720 w	690 sh		L^c
$C_3H_7-CH=CH-$	1299 s	1240 s				1150 w	1134 w			1067 m	1038 sh	947 m			841 v.w.	770 m	735 w	690 sh		L^c
$C_6H_5-CH=CH-$	1299 s	1279 s	1208 s		1180 m	1154 w		1116 w		1065 m		945 m			821 w	766 m	746 m	688 m		L^c
$CH_2=C(CH_3)-$	1233 s.b		1207 s							1092 s		971 m.b			845 m	771 m	732–727 w.b			S^d
$CH_2=C(C_2H_5)-$	1240 sh		1206 s							1098 s		951 m.b			859 m	770 m	721 v.w.b			S^d

TABLE III (*Continued*)

R_1																			
$CH_2=C(C_4H_9)—$			1208 s					1117 m		1075 s		976 v.w.[b]			854 w.b.				S[d]
$CH_2=C(C_6H_{13})—$			1206 s					1112 sh		1080 s		961 v.w.b,	912 v.w.b		856 m	771 m	721 w.b.			S[d]
$CH_2=C(C_6H_{11})—$		1225 sh	1205 s		1173 sh		1132 m			1084 s	1048 sh	959 w.b.	917 w		856 m	770 m	721 w.b.			S[d]
$C_4H_9OOCNH—\underset{CH_2}{C}—(CH_2)_7—$			1210 s				1134 w			1072 m	1040 sh				850 w	773 m				S[c]
$C_4H_9O—C(CH_3)_2—$		1251 s	1230 sh	1198 m	1182 w	1162 m		1117 w		1083 s	1035 m	948 w	899 m	871 w	843 w	773 m	737 w			S[c]
$C_4H_9NHCH(CH_3)—$	1299 w	1284 w	1227 s			1156 w	1141 w	1108 sh		1082 m	1060 w		898 w		840 w	774 m	737 w			S[c]
$C_6H_5S—CH(CH_3)—$		1246 sh	1208 s			1159 m			1085 m	1066 s			904 w		834 w	771 m	737 m	746 s	689 s	S[d]
$(C_2H_5)_2C=N—COOC_2H_5$[a]		1239 s			1170 w			1108 m		1059 w	1038 w	980 w	950 v.w	887 v.w	820 v.w	768 w	710 v.w			L[c]
$C_6H_5C(CH_3)=NCOOC_2H_5$[a]	1299 s	1235 s	1210 s		1182 sh			1124 s		1065 s										L[c]

[a] Obtained by Ref. 13 and shows Formula. [b] Measured with a calcium fluoride prism. [c] Measured by Model 21. S: solution L: liquid. [d] Measured by Model 112.

cerned in the addition reactions was not contained in up to 60–80% conversion. The addition reactions of mercaptans are greater than those of alcohols—e.g., thiophenol added exothermically to butyl *N*-vinyl carbamate to produce the saturated compound. The addition reactions of mercaptans or phenols with *N*-1-alkenyl thiocarbamates or phenyl *N*-1-alkenyl carbamates proceed more rapidly than the reactions of the corresponding 1-alkenyl isocyanates with mercaptans or phenols. When 1-alkenyl isocyanate was used in excess to another reagent, the saturated compounds were obtained.[7] All of the compounds obtained from the addition reactions mentioned above had amide bands I and II, and C=C and C=N stretching bands had disappeared. The product which was obtained from the reaction of butyl *N*-vinyl carbamate with *n*-butylamine had amide bands I, II, and no C=C band. This fact shows that no aminolysis of the carbamate group takes place and that the addition of the amine to the C=C double bond occurs.

It was reported by J. Hoch[13] that the compounds of type B were obtained from the reactions of ethyl carbamate with the corresponding ketone diethylals. The infrared spectra of *N*-carboethoxydiethylketimine and *N*-carboethoxyphenylmethylketimine were measured and are shown in Table III. The NH stretching band can be found for both compounds. Therefore, it is evident both compounds are a mixture of type A and B.

N-1-Alkenyl-N′-butylureas and N-1-alkenyl-N′-dibutylureas. Though a number of the papers[25,29–33] concerned with the spectra of urea derivatives have been presented, it is not possible to interpret fully the intricacies of the results and there are different opinions for the assignment of amide band II.[25,30] However, all urea derivatives have the amide band I arising from the CO group and those which possess at least one hydrogen atom at the nitrogen atom of the urea linkage have the amide band II arising from the NH deformation. Boivin and his co-worker have measured the infrared spectra of the types of $CH_3NHCONHR$, and concluded that these compounds had an amide band I in 1620–1660 cm.$^{-1}$ and an amide band II in 1580–1630 cm.,$^{-1}$ respectively. The spectra of *N*-ethyl-*N′*-butylurea and *N*-phenylethyl-*N′*-butylurea were measured. The former had an amide band I at 1615 cm.$^{-1}$ and an amide band II at 1580 cm.$^{-1}$ and the latter had the bands at 1620 cm.$^{-1}$ and 1582 cm.$^{-1}$, respectively. Then the infrared spectra of the types of $R_1CH=\overset{R_2}{\overset{|}{C}}—NHCONHC_4H_9$ were also measured.

---

(29) J. L. Boivin and P. A. Boivin, *Can. J. Chem.*, **32**, 561 (1954).

(30) H. J. Becher, *Ber.*, **89**, 1593 (1956).

(31) H. J. Becher and F. Griffel, *Ber.*, **91**, 2025 (1958).

(32) A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **78**, 1467 (1957).

(33) H. A. Staab, *Ann.*, **609**, 75; 83 (1957).

TABLE IV. INFRARED SPECTRA OF $R_1NHCONHC_4H_9$, CM.$^{-1}$

R_1																	
$C_2H_5—$		3320 s	2920 s		1620 s	1582 s	1515 w.sh			1460 m		1376 w			1264 w	1238 m	
$C_6H_5CH_2CH_2—$		3320 s	2925 s		1615 s	1580 s	1513 w	1500 v.w.	1472 w	1463 m		1380 w		1300 w	1275 w	1238 m	
$CH_2{=}CH—$	3420 m	3370 m	2960 s	1666 s	1638 s	1583 s				1464 m		1378 m		1287 w	1276 w	1242 s	
$CH_3CH{=}CH—$	3420 m	3370 m	2960 s	1697 m	1643 s	1582 s	1515 v.w.			1463 m		1378 m		1296 w	1287 w	1238 m	
$C_6H_5CH{=}CH—$	3420 m	3370 m	2970 s	1681 s	1640 s	1575 s	1525 v.w.		1490 m	1463 m		1378 m			1278 s	1248 s	
$CH_2{=}\underset{CH_3}{\underset{\mid}{C}}H—$		3345 m	2960 m	1670 sh	1639 s	1561 s				1465 s	1442 sh	1378 m				1242 m	
$CH_2{=}\underset{C_2H_5}{\underset{\mid}{C}}—$		3320 m	2955 m	1656 sh	1636 s	1555 s				1462 m	1443 sh	1379 m			1265 m		
$C_4H_9NHCONH\underset{CH_2}{\underset{\Vert}{C}}(CH_2)_7—$		3320 m	2920 m		1643 s	1573 s				1462 m	1437 sh	1376 w	1336 w		1263–48 m		
$C_2H_5—$			1155 w			1068 w		1025 w			908 w		770 w	740 w			Nujol, m.p. 58°
$C_6H_5CH_2CH_2—$														745 w	696 m		Nujol, m.p. 73°
$CH_2{=}CH—$	1184 w		1150 w						977 m	936 w	900 w	828 m		742 m			Nujol, m.p. 95–96°
$CH_3CH{=}CH—$	1184 w		1150 w	1130 w		1082 w		1028 w		947 m				740 m			Nujol, m.p. 108°
$C_6H_5CH{=}CH—$	1187 m	1117	1155 v.w.	1133 v.w.	1097 w	1072 w	1034 w	1028 w		950 s	899 w	822 w	753 m	743 s	688 s		Nujol, m.p. 112°
$CH_2{=}\underset{CH_3}{\underset{\mid}{C}}H—$			1147 m										755 w				Sandwich
$CH_2{=}\underset{C_2H_5}{\underset{\mid}{C}}—$			1150 w						995 w			834 w	755 w				Sandwich
$C_4H_9NHCONH\underset{CH_2}{\underset{\Vert}{C}}(CH_2)_7—$			1158 w														Solution in CCl_4

INFRARED SPECTRA OF $R_1NHCON(C_4H_9)_2$, CM.$^{-1}$

$CH_2{=}CH—$		3330 m	2950 s	1663 sh	1625 s	1530 sh		1488 s		1460 sh	1420 s	1375 m			1285 s	1233 s
$CH_3CH{=}CH—$		3330 m	2950 s	1680 m	1628 s	1530 s	1513 s	1488 s		1460 m	1408 m	1372 m			1290 m	1222 s
$C_6H_5CH{=}CH—$		3300 m	2950 s	1670 s	1632 s		1518 s	1489 s		1457 s	1400 m	1374 s		1303 m	1265 m	1245 m
$CH_2{=}\underset{CH_3}{\underset{\mid}{C}}—$		3360 m	2960 s	1668 sh	1645 s		1515 s	1485 s		1465 m	1420 m	1368 m		1290 m	1248 m	1218 s

TABLE IV (*Continued*)

R_1																	
$CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}$ heated at 100° (1 hr.)		—	2960 s	1668 sh	1645 s		—	—		1462 m	1420 m	1370 m		1290 m	1248 m	1218 s	
$CH_2{=}\underset{\underset{C_4H_9}{\vert}}{C}{-}$ heated at 50° 2 hr.		—	2970 s	1668 sh	1648 s		—	—		1463 s	1420 s	1370 s		1290 m	1250 m	1220 s	
$CH_2{=}CH{-}$	1190 sh		1150 w	1108 m		1076 w			980 m	930 w	870 w	837 m	760 w	729 w			Sandwich
$CH_3CH{=}CH{-}$	1195 sh		1155 m	1103		1053 w	1043 w			954 m							Sandwich
$C_6H_5CH{=}CH{-}$	1177 m																Nujol, m.p. 110–111°
$CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}$	1198 sh		1155 m	1110 m	1090 m			1018 v.w.		938–30 w		835 m		745 m			Liquid
$CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}$ heated at 100° (1 hr.)	1198 sh		1155 m	1108 m				1018 v.w.		938–30 w		835 m		745 m			Liquid 100° 1 hr.
$CH_2{=}\underset{\underset{C_4H_9}{\vert}}{C}{-}$ heated at 50° 2 hr.	1191 m		1151 m	1106 m				1001 v.w.		936 w		835 w		730 w			Liquid

All the compounds examined had an amide band II in 1555–1583 cm.$^{-1}$ at the same region as the two compounds above, but a different band appeared near an amide band I. *N*-Vinyl-*N'*-butylurea had two strong bands at 1638 cm.$^{-1}$ and 1666 cm.$^{-1}$, and *N*-propenyl-*N'*-butylurea had a strong band at 1643 cm.$^{-1}$ and a medium band at 1697 cm.$^{-1}$ *N*-1-Ethylvinyl-N'-butylurea had a strong band at 1640 cm.$^{-1}$ with a shoulder at 1670 cm.$^{-1}$, and when it was heated at 100° (three hours) in a tube the shoulder shifted to 1680 cm.$^{-1}$ and its intensity increased more remarkably than the band at 1640 cm.$^{-1}$ It seems reasonable to assign the strong band at 1638–1643 cm.$^{-1}$ to an amide band I, as the amide band I is strong and the position has no remarkable difference with *N,N'*-disubstituted ureas.[29,30,33] But it is impossible to assign the other band as a C=C or C=N stretching band, because both bands arise in same region. If the urea derivatives are changed to the type of $R_1CH{=}\overset{\overset{R_2}{\vert}}{C}{-}NHCON(C_4H_9)_2$, NH stretching and deformation bands should disappear in type B or the intensities of both bands should vary more noticeably than in $R_1CH{=}\overset{\overset{R_2}{\vert}}{C}{-}NHCONHC_4H_9$, because the latter has two NH groups and one nitrogen atom of them would not be concerned in the isomerization reaction. Therefore, the spectra of the compounds in this type and those after heating were measured as shown in Table IV.

In some of these spectra a strong band conceived to be an amide band II shifted remarkably towards low frequency and in some cases this band was not found. The other band conceived to be an amide band I appeared in all cases at the same position as *N,N'*-disubstituted alkylureas and *N*-1-alkenyl-*N'*-butylureas. In addition to these two bands all the spectra had a new band. *N*-Vinyl-*N'*-dibutylurea had a broad complicated strong band near 1500 cm.$^{-1}$ and a strong band at 1625 cm.$^{-1}$ with a shoulder at 1663 cm.$^{-1}$ *N*-Propenyl-*N'*-dibutylurea had a strong triplet band near 1500 cm.$^{-1}$, a strong band at 1628 cm.$^{-1}$ and a medium band at 1680 cm.$^{-1}$ *N*-Phenylvinyl-*N'*-dibutylurea also had a strong doublet band near 1500 cm.$^{-1}$ and two strong bands at 1632 cm.$^{-1}$ and 1670 cm.$^{-1}$ More interesting facts were obtained in *N*-isopropenyl-*N'*-dibutylurea and *N*-1-butylvinyl-*N'*-dibutylurea —*i.e.*, in the former an evident difference arose between two spectra (see Fig. 2). One was obtained for a sample produced by mixing two reagents (isopropenyl isocyanate and dibutylamine) at ice cooled temperature followed by distillation of excess isocyanate and solvent *in vacuo*, and the other was obtained for a sample produced by heating the former at 100° in a tube. The spectrum of the former had a NH stretching band at 3360 cm.$^{-1}$

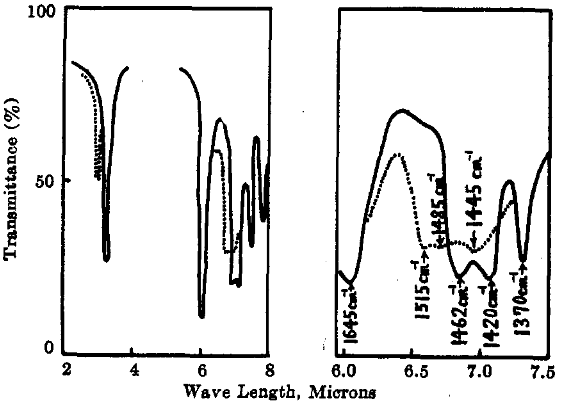


Fig. 2. Change of infrared spectrum of *N*-isopropenyl-*N'*-di-*n*-butylurea
……, before heating
———, after heating at 100° (1 hr.)

and a complicated band near 1500 cm.,$^{-1}$ and in the latter these two bands disappeared. In *N*-1-butylvinyl-*N'*-dibutylurea these two bands also disappeared in the spectrum of the material obtained by mixing two reagents at ice cooled temperature and then distilling excess isocyanate and solvent at 50° *in vacuo.* From these results it is evident that the band near 1500 cm.$^{-1}$ is due to the NH deformation (amide band II) and subsequently *N*-1-alkenylureas which possess a substitutuent at α-position of alkenyl group isomerize easily into type B. The other strong band in type $R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}NHCONHR_3$ and $R_1CH{=}\overset{R_2}{\overset{|}{C}}{-}NHCON(C_4H_9)_2$ was in the same region as the amide band I of disubstituted urea derivatives examined by other authors.[29,30,33] Therefore, this band was assigned to the amide band I arising from the CO group. The band near this band was assigned to the C=N stretching band, because the position was in the same as the C=N stretching band in *N*-1-alkenyl carbamates, the intensity increased when the sample was heated, and the spectra of *N*-isopropenyl-*N'*-dibutylurea and *N*-1-butylvinyl-*N'*-dibutylurea without NH stretching and deformation bands also have this band.

From the results described above, *N*-1-alkenyl ureas without a substituent at the α-position of the alkenyl group are mostly obtained in type A, in company with a small amount of type B, because when these compounds were heated at 100°, the intensity of the NH stretching band did not vary conspicuously and it is possible to polymerize them to high molecular weight compounds. On the other hand, *N*-1-alkenylureas with an alkyl (or dialkyl) group at the α-position of the alkenyl group isomerize into a ketimine form and it is impossible to obtain these compounds in pure state of type A. However, *N*-isopropenyl-*N'*-ethyleneurea[34] had a NH stretching band in the normal region and an amide band II near 1500 cm.$^{-1}$ after standing for a long time. Therefore, it seems that this compound is more stable than *N*-isopropenyl-*N'*-alkylurea and then the stability of *N*-1-(1-substituted) alkenylureas will vary with a substituent. If the R_3 group of $R_1\,CH{=}\overset{R_2}{\overset{|}{C}}{-}NHCONHR_3$ is changed, the stability of these compounds may increase and these compounds will be able to become important as monomers in polymer chemistry.

In order to explain the mechanism of the reactions of *N*-1-alkenylureas with amines, the oil-crystalline mixture which was obtained from the reaction between *N*-vinyl-*N'*-butylurea and *n*-butylamine was measured and it was found that the CH out-of-plane deformation at 977 cm.$^{-1}$ disappeared. Accordingly, it seems that the addition reaction of *n*-butylamine to the C=C double bond of alkenyl group takes place at first in the same way in which *N*-1-alkenyl carbamates react with nucleophilic reagents, and then the addition products obtained react further to produce the final products in accord with the mechanism proposed by this author, *et al.*[6]

CONCLUSION

Various 1-alkenyl isocyanates were prepared, and the NCO and C=C absorption bands in these compounds were measured. A number of the infrared spectra of 1-alkenyl carbamates and 1-alkenylureas were also measured, and the NH, CO, C=C, and C=N stretching bands and NH deformation band in these compounds and in the addition products obtained from the formers and nucleophilic reagents were determined. In these compounds the isomerization reactions between the C=C and C=N containing types were discussed and the following results were obtained: *N*-1-Alkenyl carbamates without a substituent at the α-position of the alkenyl group are in the C=C form and the compounds of this form are obtainable in pure state. *N*-1-Alkenyl carbamates with a substituent at α-position of the alkenyl group isomerize quite easily to the C=N form, but these compounds are also obtainable in relatively pure state of the C=C form under suitable conditions and can also be used as monomers. *N*-1-Alkenylureas without a substituent at α-position of the alkenyl group are present in a mixture of the C=C and C=N forms, but as the C=C form is abundant in *N*-vinyl-*N'*-alkylureas these compounds can be used as monomers. *N*-1-Alkenylureas with a substituent at α-position of the alkenyl group are unstable and isomerize to the C=N form, and therefore it is impossible to use these compounds as monomers in polymer chemistry so long as the

---

(34) K. Orita, M. Sato, and Y. Iwakura, *J. Chem. Soc Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), in press.

stability of these compounds do not increase by changing the R_3 group.

Acknowledgment. The author expresses his thanks to Prof. K. Kozima and Y. Iwakura for encouragement and helpful discussion. Thanks are also due to Mr. W. Suetaka in Tokyo Institute of Technology, Mr. T. Takenishi in Central Research Laboratory of Ajinomoto Co. and the Members in the Second Section of Government Chemical Industrial Research Institute, Tokyo, for measuring the infrared spectra.

TOKYO, JAPAN

[CONTRIBUTION NO. 188 FROM RESEARCH CENTER OF THE UNITED STATES RUBBER CO.]

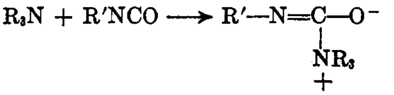
Tertiary Amine Catalysis of the Reaction of Phenyl Isocyanate with Alcohols

JOHN BURKUS

Received June 20, 1960

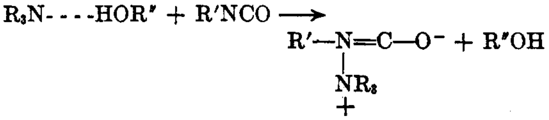
Although the rate of reaction of phenyl isocyanate with an alcohol is directly proportional to the triethylamine concentration in di-*n*-butyl ether solution, this proportionality does not hold in toluene. The relative catalytic activities of twenty-three tertiary amines were determined. These activities varied from 0.075 to 23.9. The steric requirements of the tertiary amine exert an overwhelming influence on its catalytic activity.

The reaction of isocyanates with alcohols is catalyzed by tertiary amines.[1] The possible mechanisms of base catalysis include activation of the isocyanate through the formation of a base-isocyanate complex[2a,b] and the activation of the alcohol through a base-alcohol complex.[3] The base-isocyanate complex may be formed by a direct attack of the isocyanate by the base,



$$R_3N + R'NCO \longrightarrow R'{-}N{=}\underset{\underset{+}{NR_3}}{\underset{|}{C}}{-}O^- \qquad (1)$$

and its formation by a base-alcohol complex reaction has also been suggested.[2b]



$$R_3N{-}{-}{-}{-}HOR'' + R'NCO \longrightarrow R'{-}\underset{\underset{+}{NR_3}}{\underset{|}{N}}{=}C{-}O^- + R''OH \qquad (2)$$

EXPERIMENTAL

The preparation of toluene, phenyl isocyanate, and 1-butanol and the kinetic method has been described previously.[4]

The tertiary amines, except those described below, were obtained from the commercial sources indicated in Table I. The amines were purified by conventional methods and were used immediately.

The procedure of Clarke, Gillespie, and Weeschaus[5] was used to prepare the following tertiary amines: *N,N,N',N'*-tetramethyl-1,3-propanediamine, *N,N*-dimethyl-*N',N'*-di-

TABLE I

TERTIARY AMINE CATALYTIC ACTIVITIES IN THE REACTION OF PHENYL ISOCYANATE WITH 1-BUTANOL IN TOLUENE AT 39.69°.

Catalytic activity of *N*-methylmorpholine is taken as 1.00. The amines were compared at equal amine equivalents which was about 0.0300*N*. The isocyanate and alcohol concentrations were about 0.100*M*.

Catalyst	Catalytic Activity	pK_a
N-Methylmorpholine[a]	1.00	7.41[b]
N-Ethylmorpholine[a]	0.68	7.70[b]
Ethyl morpholinoacetate	0.21	5.2[c]
Dimorpholinomethane	0.075	7.4[c]
N-(3-Dimethylaminopropyl)morpholine	2.16	
Triethylamine[d]	3.32	10.65[e]
N-Methylpiperidine[a]	6.00	10.08[e]
N,N,N',N'-Tetramethyl-1,3-propanediamine	4.15	9.8·
N,N-Dimethyl-*N',N'*-diethyl-1,3-propanediamine	3.10	
N,N,N',N',N''-Pentamethyldiethylenediamine	3.47	9.4[f]
N,N,N',N'-Tetraethylmethanediamine	0.085	10.6[c]
Bis(2-diethylaminoethyl)adipate[g]	1.00	8.6[c]
Bis(2-dimethylaminoethyl)adipate[g]	1.92	8.8[c]
N,N-Dimethylcyclohexylamine[gh]	6.00	10.1[c]
N,N-Diethylcyclohexylamine[h]	0.70	10.0[c]
N-Methyl-*N*-octylcyclohexylamine[g]	2.00	9.8[c]
N-Methyl-*N*-dodecylcyclohexylamine[g]	1.90	
N-Methyl-*N*-(2-ethylhexyl)cyclohexylamine[g]	0.16	9.6[c]
N-Methyldicyclohexylamine[g]	0.16	
1,4-Diazabicyclo(2.2.2)octane[i]	23.9	5.4[j]
1,2-Dimethylimidazole[i]	13.9	
Quinine[d]	11.3	7.8[c]
Pyridine[d]	0.25	5.29[k]

[a] From Union Carbide Chemicals Co. [b] H. K. Hall, *J. Phys. Chem.*, 60, 63 (1956). [c] Determined in this work. [d] From the Distillation Products, Ind. [e] H. K. Hall, *J. Am. Chem. Soc.*, 79, 5441 (1957). [f] R. Rometsch, A. Marxer, and K. Miescher, *Helv. Chim. Acta*, 34, 1611 (1951). [g] From the Naugatuck Chemical Co. [h] From the du Pont Co.; [i] From the Houdry Process Corp. [j] pK_b, A. Farkas and K. G. Flynn, *J. Am. Chem. Soc.*, 82, 642 (1960). [k] H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.*, 77, 4441 (1955).

---

(1) D. S. Tarbell, R. C. Mallat, and J. W. Wilson, *J. Am. Chem. Soc.*, 64, 2229 (1942).

(2) (a) J. W. Baker and J. B. Holdsworth,, *J. Chem. Soc.*, 713 (1947). (b) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9 (1949).

(3) J. F. Smith and E. C. Friedrich, *J. Am. Chem. Soc.*, 81, 161 (1959).

(4) J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, 80, 5948 (1958).

(5) H. T. Clarke, H. B. Gillespie, and S. Z. Weeschaus, *J. Am. Chem. Soc.*, 55, 4571 (1933).