bonds. An X-ray crystal-structure determination of solid hydrazine might make it possible to predict how much, if any, residual entropy is retained at low temperatures.

Heat and Free Energy of Formation of Hydrazine.—The heat of combustion of hydrazine has been studied by Hughes, Corruccini and Gilbert,[14] who report for the heat of formation of liquid hydrazine at 298.16°K., ΔH = 12,050 cal./mole. Adding to this the value of the heat of vaporization found in the present study, 10,700 cal./mole, gives for the heat of formation of hydrazine in the gaseous state at 298.16°K., ΔH = 22,750 cal./mole. Using the value of the heat content function of hydrazine from Table V and those given for nitrogen and hydrogen by Wagman, *et al.*,[12] the heat of formation at the absolute zero is calculated to be: ΔH_0^0 = 26,060 cal./mole. Using this value of ΔH_0^0 and the appropriate free-energy and heat-content functions from Table V and reference 12, values of the heat of formation, free energy of formation, and the logarithm of the equilibrium constant of formation of hydrazine were computed for various temperatures up to 1500°K. These values are given in Table VI.

TABLE VI

HEAT OF FORMATION, FREE ENERGY OF FORMATION AND LOGARITHM OF THE EQUILIBRIUM CONSTANT OF FORMATION OF HYDRAZINE

T, °K.	ΔH_f^0, kcal./mole	ΔF_f^0, kcal./mole	$\log_{10} K_f$
298.16	22.75	37.89	−27.77
300	22.74	37.98	−27.67
400	22.04	43.18	−23.59
500	21.54	48.52	−21.21
600	21.19	53.96	−19.65
700	20.95	59.44	−18.56
800	20.80	64.95	−17.74
900	20.72	70.47	−17.11
1000	20.70	76.00	−16.61
1100	20.74	81.53	−16.20
1200	20.82	87.05	−15.85
1300	20.94	92.57	−15.56
1400	21.09	98.07	−15.31
1500	21.22	103.55	−15.09

(14) Hughes, Corruccini and Gilbert, *ibid.*, **61**, 2639 (1939).

Acknowledgment.—The authors wish to acknowledge the assistance of Robert Robinson in some of the calculations of thermodynamic functions.

Summary

The heat capacity of hydrazine has been measured over the temperature range 12 to 340°K.

The vapor pressure of hydrazine has been measured over the temperature range 0 to 70°.

From the above data the entropy of the vapor at 298.16°K. was computed to be 56.97 ± 0.30 cal./deg./mole.

Using spectroscopic and molecular structure data, thermodynamic functions were calculated over the range 298.16 to 1500°K.

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

Aromatic Isocyanates as Reagents for the Identification of Some Heterocyclic Compounds

BY RONALD A. HENRY[1] AND WILLIAM M. DEHN

Since various aryl isocyanates have been applied successfully to the identification of alcohols, phenols, primary and secondary amines, a study was made to determine whether these same reagents could be used to characterize widely different heterocyclic compounds containing one or more imino groups in the ring. Previously reported solid derivatives for compounds of this type have been salts, such as picrate, picrolonate, chloroplatinate, hydrochloride, oxalate, etc.; the N-nitroso compounds have been employed in a few cases. Only a few heterocyclics of the type under consideration have been condensed with aromatic isocyanates and some of these derivatives are included in the accompanying tables. However, many of the more common heterocyclics have not been characterized previously in this manner.

In most cases these derivatives are substituted ureas; however, the presence of a carbonyl group adjacent to the imino group allows the existence of an enolic form and permits the possibility of a carbamate derivative. No effort has been made in this study to differentiate between these possibilities. The ease with which these derivatives are formed is influenced by the basicity of the heterocyclic compound. In general, the more basic the heterocyclic compound, the more rapid and complete is the reaction; or conversely, the more acidic the imino group, the less complete is the reaction, if any. As an example, pyrrole reacts very sluggishly with the isocyanates, whereas dihydro- and tetrahydropyrrole with pronounced basic properties combined vigorously.

Because of the availability of phenyl and α-naphthyl isocyanates, these compounds were employed almost exclusively in this study. The derivatives from phenyl isocyanate are the most readily obtained and recrystallized, but the reagent suffers from its susceptibility to traces of water in the compounds being identified and yields

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TABLE I

DERIVATIVES OF SOME LIQUID HETEROCYCLIC COMPOUNDS THAT CONTAIN AN IMINO GROUP IN THE RING

Compound	B. p., °C.	Mm.	Reagent[a]	M. p. of deriv., °C.[b]	N Analyses, % Calcd.	Found
Ethyleneimine	56		P	82–83[c]		
Pyrrolidine	87.5		P	133–134	14.73	14.82
Pyrrolidine			N	168.5–169.5	11.66	11.38
Pyrroline	90–91		N	203.5–204.5	11.76	11.74
Piperidine	106		P	171–172[d]		
Piperidine			N	160.5–161.5	11.02	10.98
2-Methylpiperidine	118–119		P	115.5	12.83	12.77
2-Methylpiperidine			N	179–179.5	10.44	10.33
2,6-Dimethylpiperidine	127–128		P	147[f]		
Morpholine	128		P	161.5–162	13.59	13.51
Morpholine			N	197–198	10.93	10.88
2-Methyl-1,4,5,6-tetrahydropiperidine	131–132	716	N	110–112[e]	10.51	10.42
Pyrrole	131		P	142–143	15.05	15.03
Pyrrole			T	192–194	13.99	13.85
Pyrrole			N	162–162.5	11.86	11.75
Iso-2,6-dimethylpiperidine	132–133		P	102[f]		
Pyrazoline	144		N	140–141	17.57	17.56
3-Methyl-2-pyrazoline	56	15	P	109[g]		
3,5,5-Trimethyl-2-pyrazoline	66–69	20	P	97.5–98.5	18.17	18.06
3,5,5-Trimethyl-2-pyrazoline			N	101.5–102.5	14.94	14.97
d-2-Methyl-5-ethylpiperidine	162		P	97–98[f]		
d-Coniine	168		P	72–72.5	11.37	11.30
d-Coniine			N	200–201	9.45	9.37
3-Ethyl-2-pyrazoline	76	22	P	76[g]		
3-Propyl-2-pyrazoline	82	15	P	55[g]		
Hexahydroquinoline	226	720	P	159–161[h]		
dl-2-Methylindoline	227	742	P	144–144.5		
dl-2-Methylindoline			N	163.5–164		
dl-3-Methylindoline	231	744	P	140–140.5		
2-Methyl-3,3-diethylindoline			P	149–150[i]		
1,2,3,4-Tetrahydroisoquinoline	234		P	144[j]		
1,2,3,4-Tetrahydroisoquinoline			N	144–145	9.27	9.14
1,2,3,4-Tetrahydroquinoline	251		P	96	11.10	10.96
1,2,3,4-Tetrahydroquinoline			N	162–164	9.27	9.35
1-Phenylpyrazolidine	160	20	P	114[k]		
3-Methylphenmorpholine	254–256		P	138[l]		
3-Methylphenmorpholine			N	94–95	8.80	8.72
3,5-Dimethylphenmorpholine[m]	162	35	N	134–135	8.43	8.34
2-Phenyloxazolidine	168	20	P	113–114	10.44	10.82
2-Phenyloxazolidine			N	179.5–180	8.80	8.76
2-Phenyl-4-ethyl oxazolidine	165	21	N	132	8.08	8.01
Benzothiazoline	270		P	162	10.93	11.00

[a] P = phenyl isocyanate; T = *p*-tolyl isocyanate; N = α-naphthyl isocyanate. [b] The melting points on the compounds prepared in this Laboratory have been corrected. [c] Gabriel and Stelzner, *Ber.*, **28**, 2936 (1895). [d] Gebhardt, *ibid.*, **17**, 3040 (1884). The 4-biphenyl isocyanate derivative melts at 185°, Gelderen, *Rec. trav. chim.*, **52**, 976 (1933); the *p*-nitrophenyl isocyanate derivative melts at 164°, Hoogstraten, *ibid.*, **51**, 41 (1932). [e] Forms a sticky foam at 60–70°. [f] Marcuse and Wolffenstein, *Ber.*, **34**, 2428 (1901). [g] Marie, *Bull. soc. chim.*, [4] **3**, 279 (1908). [h] Tietze, *Ber.*, **27**, 1479 (1894). [i] Ciamician and Plancher, *ibid.*, **29**, 2430 (1896). [j] Bamberger and Dieckmann, *ibid.*, **26**, 1212 (1893). [k] Michaelis and Lampe, *Ann.*, **274**, 327 (1893). [l] Stoermer and Francke, *Ber.*, **31**, 757 (1898). [m] This new compound was prepared by the method of Stoermer and Francke (previous reference) from 2-nitro-3-methylphenoxyacetone (needles from alcohol, m. p. 48–49°; calcd. for $C_{10}H_{11}NO_4$: N, 6.70. Found: N, 6.80).

the difficultly separable diphenylurea. α-Naphthyl isocyanate is less subject to an interfering hydrolysis, but some of its derivatives show a tendency to decompose on recrystallization and a gradual pyrolysis so that the melting points are not always sharp. An example of such a decomposition is found in the α-naphthyl derivative of 3,5-dimethylpyrazole: The initial reaction product obtained in absolute ether melted at 123.5–124.5°; attempted recrystallization from aqueous alcohol gave di-α-naphthylurea, ethyl N-(α-naphthyl)-carbamate, and the starting pyrazole.

Derivatives of imidazole, indazole and benzotriazole exhibit a marked tendency to dissociate in hot solutions of benzene or toluene and the intense odor of the isocyanate appears. With 4,5-

diphenylimidazole this dissociation is essentially complete in boiling toluene and the starting heterocyclic can be filtered from the hot solution.

Experimental

Because of the diverse physical and chemical properties of the heterocyclic compounds, no one general procedure was found applicable. However, the purification in most methods was simplified when the imino compound was in slight excess so that no free isocyanate remained after the reaction; this permitted the use of ordinary solvents for recrystallization. On the other hand, an excess of the isocyanate was desirable in the recrystallization of imidazole, etc., derivatives so as to prevent their dissociation.

Four procedures were developed and are described below; the first was found to be satisfactory in the majority of cases.

Procedure I: To 1.0 g. of the compound dissolved in 10 ml. of absolute diethyl ether if readily soluble or in a minimum volume of the solvent if only moderately soluble was added 0.5–0.7 g. of the isocyanate. After fifteen minutes the solid material was removed by filtration, washed once or twice with small volumes of absolute ether, and once with petroleum ether. The derivative was recrystallized rapidly from 5 to 10 ml. of ethyl alcohol, aqueous ethyl alcohol, or a mixture of acetone and ethyl alcohol.

If no solid product separated during fifteen minutes, the solution was allowed to stand overnight in a stoppered flask before separating and purifying the derivative. Occasionally, part of the solvent had to be evaporated before the derivative separated.

Procedure II: When the heterocyclic compound was only sparingly soluble in ether, it was dissolved in a minimum quantity of boiling, anhydrous benzene or toluene and refluxed with one-half to three-quarters of its weight of the isocyanate until the odor of the latter disappeared. The derivative was fractionally crystallized from the solvent and recrystallized from benzene or ethyl alcohol.

Procedure III: For compounds like cyclic imides, creatinine, pyrrole, and pyrazolones, the derivatives were prepared by heating 1.0 g. of the heterocyclic with 0.5 g. of the isocyanate at 80° without solvent until the mixture had become solid or the odor of the isocyanate had disappeared. The solid reaction cake was ground and triturated with a mixture of diethyl ether and petroleum ether (b. p. 30–80°) to remove unchanged isocyanate, and then with hot water or 5% sodium carbonate solution to remove any unchanged heterocyclic. The residue was recrystallized from ethyl alcohol, ethyl alcohol-acetone, or benzene.

This procedure also was employed with imidazoles, benzimidazoles, indazoles, and triazoles except that an excess of the isocyanate was used and the crude derivative recrystallized directly from dry toluene or benzene.

TABLE II

DERIVATIVES OF SOME SOLID HETEROCYCLIC COMPOUNDS THAT CONTAIN AN IMINO GROUP IN THE RING

Compound	M. p., °C.	Reagent[a]	M. p. of deriv., °C.[b]	N Analyses, % Calcd.	Found
Triacetonamine	34.6–34.9[c]	P	88–88.5	10.21	10.17
trans-Decahydroquinoline	48.2–48.5	P	153[d]		
Indole	52	P	136[e]	11.86	11.62
Indole		N	147–149	9.79	9.81
2-Methylindole	59–60	P	188[f]	11.19	11.16
3-Methyl-5-ethoxypyrazole	66-67	P	89–90		
3-Methyl-5-ethoxypyrazole		T	84.5–85	16.21	16.10
2-Ketohexamethylenimine	65–68	P	66–67[g]		
2-Ketohexamethylenimine		N	119–120		
Pyrazole	70	N	108.5–109.5	17.72	17.71
5-Methyl-1,2,3-benzotriazole	83–85	P	159–160[h]		
9-Methyl-9,10-dihydrophenanthridine	87.5–88.5	P	149.5–150	8.91	9.00
9-Methyl-9,10-dihydrophenanthridine		N	132–133	7.69	7.65
3,5-Diphenyl-2-pyrazoline	88	P	169[i]		
Imidazole	89–90	P	114.5–115.5	22.45	22.36
Imidazole		N	238–239[j]		
9,10-Dihydrophenanthridine	90	P	141–141.5	9.33	9.36
9,10-Dihydrophenanthridine		N	173–174	8.00	8.14
3-Methylindole	95	P	137		
3-Methylindole		N	193–194	9.33	9.23
3-Methylnaphthomorpholine	95.5	P	180[k]		
1,2,3-Benzotriazole	96–97	P	140–141	23.93	23.87
1,2,3-Benzotriazole		N	148–149	19.44	19.43
Piperazine	105–106	P	[l]		
7-Chloro-3-methylphenmorpholine	106	P	148[k]		
5-Chloromethyl-2-oxazolidone	105–106	P	154–155[m]		
3,5-Dimethylpyrazole	107	P	66.5–67	19.52	19.58
3,5-Dimethylpyrazole		N	123.5–124.5	15.84	15.66
1,2,4-Triazole	120–121	P	112–112.5	29.78	29.53
1-Phenyl-3-methyl-5-pyrazolone	127	P	142–143[n]	14.53	13.99
2,4,5-Triphenyl-2-imidazoline	131–133	P	171–172	10.07	10.12
2,4,5-Triphenyl-2-imidazoline		N	154–155	8.99	9.01
3-Phenyl-4,5,6,7-tetrahydroindazole	133	P	115–116[o]		
2-Benzoxazolone	137–138 (142)	P	125[p]		
Phthalimidine	150	P	182.5–183	11.11	11.25

TABLE II (*Continued*)

Compound	M. p., °C.	Reagent[a]	M. p. of deriv., °C.[b]	N Analyses, % Calcd.	Found
Phthalimidine		N	218–219	9.27	9.20
Benzimidazole	170	P	153–154	17.71	17.69
Benzimidazole		N	141.5–142		
2-Methylbenzimidazole	174	P	128–129	16.63	16.65
Phenothiazine	180	P	168–169		
4-Nitroindazole	181	P	207.5	19.85	19.60
4-Nitroindazole		N	262–263	16.86	16.21
3,5-Diphenylpyrazole	199	P	108	12.38	12.44
3,5-Diphenylpyrazole		T	130–131	11.89	11.90
3,5-Diphenylpyrazole		N	152–153	10.79	10.74
Isatin	200-201	P	180–185[q]		
dl-Proline	203	P	170[r]		
dl-Proline		N	171–172[s]		
5-Nitroindazole	209	P	200[t]	19.85	19.88
5-Nitroindazole		N	226.5	16.86	16.71
3-Methyl-5-pyrazolone	217	P	237–238	19.36	19.30
3-Methyl-5-pyrazolone		T	234–235	18.18	18.10
3-Methyl-5-pyrazolone		N	195	15.74	15.59
3-(2-Furyl)-5-pyrazolone	223	P	192[u]		
Saccharin	223–228	P	183	9.27	9.17
Saccharin		T	192	8.86	8.86
4,5-Diphenylimidazole	229	P	210.5		
5-Methyl-3-pyrazolecarboxylic acid	236	P	158–160	17.14	17.12
1,2,7,8-Dibenzophenothiazine	236	P	215–220[v]		
Phthalimide	238	P	146–147		[w]
Phthalimide		T	155–156		
Glycylalanine anhydride	247	P	158–159[x]		
Phenylalanyl glycine anhydride	265.5	P	154[x]		
Creatinine	260	T	197–198	22.76	22.57
Glycine anhydride	311–312	P	270[x]		

[a] P = phenyl isocyanate; T = *p*-tolyl isocyanate; N = α-naphthyl isocyanate. [b] The melting points on the compounds prepared in this Laboratory have been corrected. [c] Anhydrous material. [d] Bamberger and Lengfeld, *Ber.*, **23**, 1149 (1890). [e] Decomposes into a sticky foam at indicated temp.; m. p. 193–195. [f] Walther and Clemen, *J. prakt. Chem.*, [2] **61**, 262 (1900), report a m. p. of 170°. [g] Mixed m. p. with starting material was 42–45°. [h] Leuckart, *ibid.*, [2] **41**, 325 (1890). [i] Heilbron and Wilson, *J. Chem. Soc.*, **103**, 1511 (1913). [j] Melts at 105–110° when plunged into hot bath; resolidifies. [k] Stoermer and Francke, *Ber.*, **31**, 757 (1898). [l] No m. p. given by Rosdalsky, *J. prakt. Chem.*, [2] **53**, 21 (1896). [m] Johnson and Guest, *Am. Chem. J.*, **44**, 462 (1910). [n] Wislicenus, Elvert and Kurtz, *Ber.*, **46**, 3400 (1913), report a m. p. of 92–93°. [o] Bauer, *Ann. chim. phys.*, [9] 1, 428 (1914). [p] v. Meyer, *J. prakt. Chem.*, [2] **92**, 257 (1915). [q] Gumpert, *ibid.*, [2] **92**, 283 (1915). [r] Fischer, *Ber.*, **34**, 459 (1901). [s] Neubert, *Biochem. Z.*, **37**, 499 (1911). [t] Mixed m. p. with starting compound was 165°. [u] Torrey and Zanetti, THIS JOURNAL, **30**, 1243 (1908). [v] Paschkwetzky, *Ber.*, **24**, 2917 (1891). [w] Two analyses on this compound gave N, 12.45, 12.57 (theory, 10.52). A mixed m. p. with phenylurea (m. p. 147°, N, 20.54) was 125–130°. [x] Ludke, *Z. physiol. Chem.*, **150**, 215 (1925).

Procedure IV: For compounds containing carboxylic acid groups the method of Emil Fischer[2] was used.

The derivatives prepared by these procedures are summarized in Tables I and II. Carbazole, theobromine, barbituric acid, uric acid, 5,5-dimethylhydantoin, diethyl dihydrocollidinedicarboxylate, diethyl 2,4-dimethyl-3,5-pyrroledicarboxylate, tetraphenylpyrrole, and tetraiodopyrrole could not be made to react by any of these methods. 3-Methyl-4-isopropylidene-5-pyrazolone gave intensely red-colored solutions with the isocyanates, but no pure solid products could be isolated. Succinimide also gave a deep purple color on heating with phenyl isocyanate.

Reaction of *p*-Tolyl Isocyanate with Diphenylguanidine.—Four grams of *sym*-diphenylguanidine, slurried in 20 ml. of absolute ether, was treated with 2.6 g. of *p*-tolyl isocyanate. The solution momentarily cleared, then filled with a voluminous precipitate; a portion of this material was removed and drained on a porous plate; m. p. about 92°. It appeared to be an unstable addition compound. In about thirty minutes this original precipitate had redissolved completely; after standing several days, hard prisms of N^1,N^3-diphenyl-N^2-(*p*-tolylcarbamyl)-guanidine began to form; m. p. 133–134°. *Anal.* Calcd. for $C_{21}H_{20}ON_4$: N, 16.27. Found: N, 16.09.

The corresponding α-naphthyl derivative, rosettes of prismatic needles from ether, melted at 139–140°. *Anal.* Calcd. for $C_{24}H_{20}ON_4$: N, 14.73. Found: N, 14.61.

The phenyl derivative, recrystallized from acetone, melted at 146–147°. *Anal.* Calcd. for $C_{20}H_{18}ON_4$: N, 16.96. Found: N, 16.72.

(2) Fischer, *Ber.*, **33**, 1703 (1900); **34**, 459 (1901).

Summary

Solid derivatives, suitable for identification purposes, have been prepared by the reaction of the common isocyanate reagents with representative heterocyclic compounds containing one or more imino groups in the ring.

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