The volume of solution containing 1000 g. of solvent increases continuously as the concentration of strontium chloride increases. Also the rate at which this volume increases with respect to the concentration (partial molal volume) is greatest for the solvent containing 60% ethanol. The apparent molal volume of strontium chloride in a given solvent is greatest in the most concentrated solution. This indicates, for these systems, that for a given solvent the extent of solvation for the individual ions is least when the largest number of ions is present or when the number of solvent molecules for each ion is least. (The ion–solvent complex should be less compact or smaller in size if the solvent dipoles have been partially reduced by the presence of other ions in the solution and the greater this reduction the less the extent of solvation and the greater the apparent molal volume). This may be observed from Fig. 1. It may also be noted from Fig. 1 that the apparent molal volume of strontium chloride (for each concentration) reaches a maximum when the solvent contains about 60% ethanol. At points where these maxima are reached the degree of solvation should be least with greater solvation occurring both above and below these points.

Summary

1. The densities of solutions of strontium chloride in different mixtures of ethanol and water at 25° have been determined.

2. The apparent molal volumes of strontium chloride in mixtures of ethanol and water have been calculated and the results discussed.

3. The apparent molal volumes of strontium chloride in ethanol–water mixtures exhibit a maximum in solutions containing about 60% ethanol and this volume is greatest in the most concentrated solutions.

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[CONTRIBUTION NO. 15 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions[1]

BY D. W. SCOTT, G. D. OLIVER,[1a] MARGARET E. GROSS, W. N. HUBBARD AND HUGH M. HUFFMAN

Because of the potential use of hydrazine as a rocket propellant, a knowledge of its thermodynamic properties is of considerable importance. Consequently, the Thermodynamics Laboratory of the Petroleum and Natural-Gas Branch of the Bureau of Mines has undertaken the measurement and computation of certain of these properties. This paper reports the results of calorimetric and vapor-pressure measurements which yield a value of the entropy of hydrazine vapor and also presents a tabulation of various thermodynamic functions calculated from spectroscopic and molecular structure data.

Experimental

Heat Capacity.—The measurements were made in the adiabatic calorimeter apparatus first described by Ruehrwein and Huffman.[2] The hydrazine used for this work was obtained from the Western Cartridge Co. through the courtesy of R. L. Womer, and as received had a purity of about 99.2 mole per cent., the major contaminant being water. It was further purified by refluxing over barium oxide, followed by repeated fractional crystallization. From a study of the melting point as a function of the fraction melted the purity of the sample was estimated to be 99.75 mole per cent. The melting point of the actual sample was found to be 274.56°K. and that calculated for the pure material was 274.69°K.

In the heat capacity measurements, the absorption of a small amount of heat (about 8 cal./mole) was observed to occur near 220°K. This presumably resulted from the melting of a eutectic mixture of hydrazine and hydrazine monohydrate formed from water impurity in the sample. Semishin,[3] who studied the freezing-point behavior of the hydrazine–water system, was unable to measure this eutectic temperature because of excessive supercooling, but any reasonable extrapolation of his freezing point curves at higher temperatures gives an intersection at about the temperature where this absorption of heat was observed.

The precision of the calorimetric measurements was approximately 0.1% above 30°K., but because of the relatively impure sample used and certain difficulties encountered in the measurements, the absolute uncertainty of the heat-capacity values may be as great as 0.3%. Because the heat-capacity data are less accurate than is usual for this type of work and because the true course of the heat-capacity curve between about 200°K. and the melting point is obscured by the premelting effect, it seemed desirable to report only the smoothed values of heat capacity at integral temperatures. These are listed in Table I. Two concordant values were obtained for the heat of fusion. After applying approximate corrections

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(1) Not subject to copyright.

(1a) Present address: Carbide & Carbon Chemicals Corp., Oak Ridge, Tenn.

(2) Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

(3) Semishin, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 654 (1938).

for premelting and the heat required to melt the eutectic mixture, the value taken for the heat of fusion was 3,025 cal./mole. This value has a large absolute uncertainty, since the premelting correction depends on the arbitrarily assumed course of the heat capacity curve below the melting point. However, this uncertainty will have little effect on the entropy calculated from these data.

TABLE I

HYDRAZINE, SMOOTHED HEAT CAPACITY, CAL./DEG./MOLE

T	$C_{\text{sat.}}$	T	$C_{\text{sat.}}$	T	$C_{\text{sat.}}$
12	0.070	70	5.145	220	13.030[a]
13	.095	75	5.560	230	13.445[a]
14	.115	80	5.965	240	13.865[a]
15	.140	85	6.355	250	14.280[a]
16	.165	90	6.720	260	14.700[a]
17	.205	95	7.060	270	15.120[a]
18	.250	100	7.375	274.69	15.310[a]
19	.300	110	7.980	Liquid	
20	.350	120	8.540	274.69	23.29
25	.680	130	9.070	280	23.37
30	1.105	140	9.570	290	23,51
35	1.605	150	10.045	298.16	23.62
40	2.130	160	10.600	300	23.65
45	2.675	170	10.935	310	23.80
50	3.215	180	11.360	320	23.96
55	3.740	190	11.775	330	24.14
60	4.230	200	12.195	340	24.34
65	4.700	210	12.610[a]		

[a] Extrapolated.

Vapor Pressure and Heat of Vaporization.—The vapor pressure of hydrazine was studied over the temperature range 0–70° by a static method. The apparatus and methods were similar to those described in a prior publication from this Laboratory.[4] A 5-ml. portion of the same material that was used for the low-temperature studies was employed for the vapor-pressure measurements. The usual test for purity of the sample—comparing vapor pressures measured after pumping off different amounts of the original material—showed that the vapor pressure was affected significantly by the small amount of water which the heat-capacity studies had indicated to be present in the sample. A set of measurements made after about 20% of the original sample was pumped off (Series I) gave values several tenths of a per cent. higher than a second set of measurements made after having pumped off about 80% of the original sample (Series II). Since hydrazine and water form a maximum-boiling azeotrope, the effect of water as an impurity in hydrazine is to make the vapor pressure *less* than that of pure hydrazine. Qualitative considerations of the vapor–liquid equilibrium in the hydrazine–water system suggested the possibility of obtaining a purer sample of hydrazine by a simple bulb-to-bulb distillation. Consequently, the entire 5-ml. portion of hydrazine was transferred to a storage bulb, and about 20% of it was then distilled under its own vapor pressure back into the sample container. A third set of measurements (Series III), made with this 20% of the original material, did yield values of the vapor pressure somewhat higher than those obtained in either of the two previous series. The vapor-pressure data obtained in all three sets of measurements are tabulated in Table II.

TABLE II

VAPOR PRESSURE OF HYDRAZINE

t, °C.	Observed vapor pressure, mm. Series I	Series II	Series III	Calcd. Eq. 1
0	2.60[a]	2.57[a]	2.60[a]	
0	2.64[b]	2.64[b]	2.69[b]	2.67
15	7.55	7.51	7.65	7.64
20	10.45	10.41	10.55	10.53
25	14.27	14.22	14.38	14.35
30	19.25	19.16	19.29	19.31
35	25.54	25.50	25.67	25.70
40	33.71	33.63	33.82	33.83
45	43.91	43.81	44.08	44.10
50	56.78	56.61	56.91	56.93
55	72.63	72.48	72.85	72.84
60	92.24	91.99	92.43	92.40
65	116.10	115.75	116.30	116.26
70	144.92	144.58	145.12	145.16

[a] Solid. [b] Supercooled liquid.

Since the sample used for Series III was presumably of somewhat higher purity than those used for either of the two previous sets of measurements, the vapor-pressure data obtained in this latter series were used to calculate the heat of vaporization at 298.16°K. An Antoine equation was fitted to the data of Series III by a least-squares adjustment,[5] and the equation obtained was

$$\log_{10} P = 7.80687 - 1680.745/(t + 227.74) \qquad (1)$$

Values calculated by means of this equation are listed in column 5 of Table II for comparison with the data of Series III. The heat of vaporization calculated from equation (1), using the Berthelot equation of state and critical point data,[6] is 10,700 cal./mole, with an estimated uncertainty of ±75 cal./mole. Values of the heat of vaporization calculated in the same manner from the data of Series I and of Series II agree with this value within the assigned limits of uncertainty.

Vapor-pressure data for hydrazine have previously been reported by Hieber and Woerner.[7] A comparison of the values found in this investigation with those reported by Hieber and Woerner is made in Fig. 1, where the per cent. deviation of the observed pressures from the values given by equation (1) is plotted *vs.* temperature. Where the two sets of measurements overlap, the values re-

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(4) Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, THIS JOURNAL, **71**, 797 (1949).

(5) Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(6) de Bruyn, *Rec. trav. chim.*, **15**, 174 (1896).

(7) Hieber and Woerner, *Z. Elektrochem.*, **40**, 252 (1934).

ported by Hieber and Woerner are consistently lower than those found in this work, a fact which suggests that the sample used by these earlier investigators contained a higher concentration of water than the one used in the present study.

Entropy.—The entropy of hydrazine was calculated from the calorimetric and vapor-pressure data in the usual manner. This calculation is summarized in Table III.

TABLE III

ENTROPY OF HYDRAZINE IN CAL./DEG./MOLE

0–12°K.	Extrapolation (T^3 law)	0.02	
12–274.69°	Solid, graphical	16.03	
274.69°	Fusion (3025/274.69)	11.01	
274.69–298.16°	Liquid, graphical	1.91	
	Entropy of liquid at 298.16°K.		28.97 ± 0.10
298.16°	Vaporization (10,700/298.16)	35.89	
298.16°	Compression (R ln 14.35/760)	−7.89	
	Entropy of ideal gas at 298.16°K. and 1 atm.		56.97 ± 0.30

Thermodynamic Functions from Spectroscopic and Molecular Structure Data

The Raman and infrared spectra of hydrazine have been studied by a number of investigators.[8] Some of the more recent spectroscopic data are listed in Table IV. As discussed by Fresenius and Karweil,[8d] the spectra indicate that the stable configuration of the hydrazine molecule with respect to rotation about the N–N single bond is not the *trans*-configuration but a less symmetrical form of C_2-symmetry. The number of coincidences between Raman lines and infrared bands is consistent with the C_2-form, for which the selection rules permit all frequencies to appear in both spectra, but not with the *trans*-form, for which all coincidences are forbidden. All of the observed frequencies can be satisfactorily accounted for on the basis of the C_2-structure alone. If the *trans*-configuration can exist as a metastable tautomer, it must have an energy several thousand calories above that of the C_2-configuration; otherwise, additional vibrational frequencies arising from the *trans*-modification would have been observed in the spectra. (The *cis*-configuration, while not seriously in conflict with the spectroscopic data, is not considered here, since it requires the hydrogen atoms to have the opposed rather than the staggered configuration.)

TABLE IV

SPECTRA[a] AND VIBRATIONAL ASSIGNMENT FOR HYDRAZINE

Raman[b] (liq.)	Infrared (liq.)[c]	Infrared (gas)[d]	Assignment
101 (1)			Liquid structure?
513 (1)			876 − 360 = 516
749 (0)			1108 − 360 = 748
802 (2)		815 (2)	NH_2 wagging
		850 (2)	
876 (6)	885		N–N stretching
943 (1)		930 (10)	NH_2 wagging
995 (1)		965 (10)	
1108 (8)	1097	1082 (1)	NH_2 rocking
1199 (0)		1165 (0)	NH_2 rocking
1316 (1b)	1324	1282 (3)	NH_2 bending
1618 (5)	1613	1585 (7)	NH_2 bending

[a] Below 1700 cm.$^{-1}$. [b] Goubeau, ref. 8e. [c] Krivich, ref. 8f. [d] Fresenius and Karweil, ref. 8d.

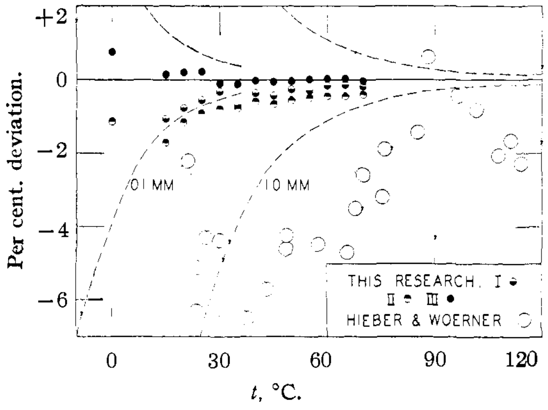

Fig. 1.—Deviation plot of the vapor pressure data for hydrazine of this research and of Hieber and Woerner, ref. 7. The base line is eq. (1). The dotted lines indicate the per cent. deviations corresponding to absolute deviations of 0.1 and 1.0 mm.

The vibrational assignment proposed here differs somewhat from that made previously by Fresenius and Karweil.[8d] In particular, it is necessary to take account of the fact that the two NH_2 wagging modes are double minimum vibrations and give rise to doublets in the spectra. These are observed in the infrared at 815 and 850 cm.$^{-1}$ and at 930 and 965 cm.$^{-1}$. Corresponding Raman lines are observed for all except the higher frequency component of the first doublet, which apparently is not resolved from the stronger N–N stretching frequency at 876 cm.$^{-1}$.

The number of observed frequencies between 1000 and 1600 cm.$^{-1}$ are just enough to account for the four NH_2 vibrations whose frequencies would be expected to occur in this range. The spectrum in the region of the N–H stretching frequencies (3000–3400 cm.$^{-1}$) is complicated by resonance interaction with the overtone of the 1585 cm.$^{-1}$ frequency, and no definite assignment was attempted for the four N–H stretching fundamentals. For purposes of thermodynamic calculations, an adequate approximation is to use the frequencies of the four infrared bands found in this region, 3160, 3255, 3285 and 3360 cm.$^{-1}$. Also, for thermodynamic calculations, it is permissible to treat the double minimum vibrations as harmonic oscillations with frequencies equal to the mean of the observed doublets.

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(8) (a) Sutherland, *Nature*, **126**, 916 (1930); (b) Imanishi, *Sci. Pap. Inst. Tokyo*, **16**, 1 (1931); (c) Kahovec and Kohlrausch, *Z. physik. Chem.*, **B38**, 96 (1937); (d) Fresenius and Karweil, *ibid.*, **B44**, 1 (1939); (e) Goubeau, *ibid.*, **B45**, 237 (1940); (f) Krivich, *Compt. rend. acad. sci. U. S. S. R.*, **23**, 36 (1939).

Stevenson and McMahon[9] found in the case of ammonia that such a treatment gave results practically identical with those obtained by summing over the individual energy levels. The complete set of vibrational frequencies used for the thermodynamic calculations is as follows: 833, 876, 948, 1082, 1165, 1282, 1585, 3160, 3255, 3285 and 3360 cm.$^{-1}$.

The frequency of the torsional oscillation about the N–N single bond has not been observed directly, although it is permitted by the selection rules. However two weak Raman lines at 513 and 749 cm.$^{-1}$ are apparently difference-combinations arising from a torsional frequency of about 360 cm.$^{-1}$. No other way was found to account for these two observed Raman lines.

Since the detailed shape of the potential barrier to internal rotation is not known, some reasonable approximation must be made for purposes of thermodynamic calculations. The barrier, V, adopted is given by the following relations

$$\begin{aligned} V &= (^1/_2)(1 + \cos 3\,\theta)\ 2800\ \text{cal./mole} \left\{\begin{array}{l} 0° < \theta < 120° \\ 240° < \theta < 360° \end{array}\right. \\ &= 2800\ \text{cal./mole} \qquad\qquad\qquad\qquad 120° < \theta < 240° \end{aligned} \tag{2}$$

where θ is the angle of internal rotation measured from the *cis*-configuration. The two minima at $\theta = 60°$ and $\theta = 300°$ correspond to the two optical isomers of the stable C_2-configuration, and the barrier height of 2800 cal./mole is that required to give a torsional frequency of 360 cm.$^{-1}$. The assumption of constant rotational potential energy between $\theta = 120°$ and $\theta = 240°$ is a rough approximation consistent with the fact that the energy of the *trans*-configuration ($\theta = 180°$) is considerably higher than that of the C_2-configuration. The details of the barrier in this region are relatively unimportant for thermodynamic purposes.

For calculating the moments of inertia, the following bond distances and angles were used: N–N distance, 1.47 Å.; N–H distance, 1.04 Å.; all bond angles tetrahedral; and the two NH_2 groups rotated 60° from the *cis*-configuration. The bond distances are from the electron diffraction study of Giguere and Schomaker.[10] The calculated moments of inertia are: 6.18×10^{-40}, 35.33×10^{-40} and 36.98×10^{-40} g. cm.^{2}; the axis of least moment of inertia makes an angle of 3° 30′ with the N–N bond. The reduced moment for internal rotation, calculated by Pitzer's formula for an unsymmetrical top attached to a rigid frame[11] is 1.53×10^{-40} g. cm.^{2}. The symmetry number of hydrazine is 2.

The contributions of translation, over-all rotation and vibration to the thermodynamic functions were computed in the usual manner. Only the contributions of internal rotation resulting from the potential barrier, eq. (2), require special comment. Because of the low reduced moment of inertia for internal rotation, it was not permissible to use the classical partition function. What was done was to treat the problem as an equilibrium between the C_2-form of hydrazine, whose internal rotation is hindered by a barrier of 2800 cal./mole, and the *trans*-form, having free internal rotation. The energy difference between the two forms (ΔE^0_0) is 2800 cal./mole less the zero point energy of the C_2-form, 540 cal./mole. The *trans*-form and the two optical isomers of the C_2-form are each limited to one third of a revolution. The same partition functions for vibration and overall rotation were used for the *trans*-form as for the C_2-form, since changes in vibrational frequencies tend to compensate for changes in the moments of inertia in the complete partition function.[11]

Values of the free-energy function, heat-content function, entropy and heat capacity of hydrazine were computed for selected temperatures up to 1500°K., using the vibrational assignment and structural parameters given previously. The values of the physical constants given by Wagman, *et al.*,[12] and 1948 atomic weights were used in the calculations. The thermodynamic functions are listed in Table V. Some values in the table are given to more significant figures than is justified by their absolute accuracy, in order to retain internal consistency among the different functions.

TABLE V

THERMODYNAMIC FUNCTIONS FOR HYDRAZINE

T, °K.	$(H^0_0 - F^0_T)/T$, cal./deg./mole	$H^0_T - H^0_0$, kcal./mole	S^0_T, cal./deg./mole	C^0_p, cal./deg./mole
298.16	47.98	2.812	57.41	12.6
300	48.04	2.835	57.49	12.6
400	50.91	4.221	61.46	15.1
500	53.39	5.823	65.03	16.9
600	55.59	7.584	68.23	18.3
700	57.61	9.482	71.16	19.5
800	59.47	11.48	73.83	20.6
900	61.21	13.59	76.31	21.5
1000	62.84	15.78	78.62	22.3
1100	64.37	18.06	80.79	23.1
1200	65.83	20.41	82.83	23.9
1300	67.21	22.83	84.77	24.5
1400	68.53	25.31	86.60	25.1
1500	69.80	27.80	88.35	25.5

The calculated value of the entropy at 298.16°K. is 0.44 cal./deg./mole higher than that observed calorimetrically. This difference is less than the combined uncertainty of the calorimetric and calculated values and may not be significant. However, it suggests the possibility that some randomness of orientation exists in solid hydrazine at low temperatures, leaving residual entropy not included in the calorimetric value. Such a situation is known to exist in ice,[13] and may well occur in other crystals having strong hydrogen

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[9] Stevenson and McMahon, This Journal, **61**, 437 (1939).

[10] Giguere and Schomaker, *ibid.*, **65**, 2025 (1943).

[11] Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

[12] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[13] Pauling, This Journal, **57**, 2680 (1935).

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., $\Delta H = 12{,}050$ 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., $\Delta H = 22{,}750$ 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: $\Delta H_0^0 = 26{,}060$ 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

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.

BARTLESVILLE, OKLAHOMA RECEIVED FEBRUARY 17, 1949

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

[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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