671. *Nitramines and Nitramides. Part V.* Nitrations of Urethane,* N-*Methylurethane, Urea, and Hexahydro*-1 : 3-*dinitro*-1 : 3 : 5-*triazine in Sulphuric Acid.*

By C. HOLSTEAD, ALEX. H. LAMBERTON, and (in part) P. A. H. WYATT.

The nitrations of urethane, *N*-methylurethane, urea, and hexahydro-1 : 3-dinitro-1 : 3 : 5-triazine are reversible in sulphuric acid–water media; the position of equilibrium depends on the concentration of the acid. For urea and the hexahydrotriazine, as for guanidine (Simkins and Williams, *J.*, 1952, 3086), nitration reaches its maximum in 88% w/w sulphuric acid. The urethanes, however, show an increasing degree of nitration, though the equilibrium is established more slowly, as the acid concentration is decreased (88 ⟶ 75%, w/w). This difference (as between urea and urethane) may be due to differing degrees of salt formation, but neither cryoscopic measurements nor ultra-violet spectra provide proof.

IN Part III (*J.*, 1952, 1886) we gave the qualitative results of the treatment of a wide variety of *N*-nitro-compounds with sulphuric acid. By arrangement with Professor Gwyn Williams, of whose work we learnt during the earlier research, we examined quantitatively a number of nitrations, but left the detailed investigation of the nitration of guanidine in sulphuric acid (Part I, Simkins and Williams, *J.*, 1952, 3086) to his laboratory.

In general, we added the *N*-nitro-compound to sulphuric acid–water mixtures of known composition, and determined, by the method of Simkins and Williams (*loc. cit.*), the nitric acid liberated. In some cases, to prove reversibility, we employed equimolar quantities of the amide and nitric acid, or a salt [*e.g.*, urea nitrate or hexahydro-1 : 3-dinitro-1 : 3 : 5-triazine nitrate (" P.C.X.") (I)] as initial materials. Minor modifications in technique are detailed in the Experimental section.

After dissolution of nitrourethane (0·2M) in a sulphuric acid–water mixture (75·4% H_2SO_4, w/w), the free nitric acid in the system rose, in about 5 hours at 25°, to 39% of the total potentially available. When equimolar quantities (0·2M) of urethane and nitric acid were used initially, the free nitric acid fell, in the same time, to 37% of its initial value. The equilibrium values are not precisely identical, since the nitric acid was added as concentrated (70% w/w) acid: the water thus introduced changed the initial solvent to 74·6% w/w sulphuric acid. In more concentrated acid equilibrium was established more rapidly. In 79·9% w/w sulphuric acid equilibration was complete in 40 minutes, whilst in 91·5% w/w sulphuric acid it was attained before the first observation was made (14 minutes after mixing).

In concentrated sulphuric acid the nitric acid content of the equilibrium mixtures fell slowly; this appears to be due to the irreversible decomposition of the *N*-nitro-compound to yield nitrous oxide. The reaction is distinct from, but concurrent with, the nitration–denitration equilibrium, and is under investigation. To allow for the loss of nitric acid occasioned indirectly by the irreversible decomposition of the *N*-nitro-compound, the experimental curves were extrapolated back to the time origin, and the figures thus obtained taken to indicate the true equilibrium proportion of free nitric acid in 0·2M-solutions at 25°. As nitric acid is stable, and the *N*-nitro-compound unstable, this is presumably an under-correction (*i.e.*, will not indicate sufficient nitric acid) whenever the *N*-nitro-compound was used as initial material; but, with three exceptions (indicated specifically in the Experimental section), we do not believe the error in the correction to be significant.

The Figure shows how the equilibrium proportions of nitric acid (evaluated, as indicated above, by extrapolation to zero time) varied with changes in the sulphuric acid–water solvent. It will be seen that urea (curve I), like guanidine (curve II, plotted from the results of Simkins and Williams, *loc. cit.*), showed a maximum degree of nitration in the optimum solvent (88% w/w sulphuric acid) for aromatic nitration, though the yield from

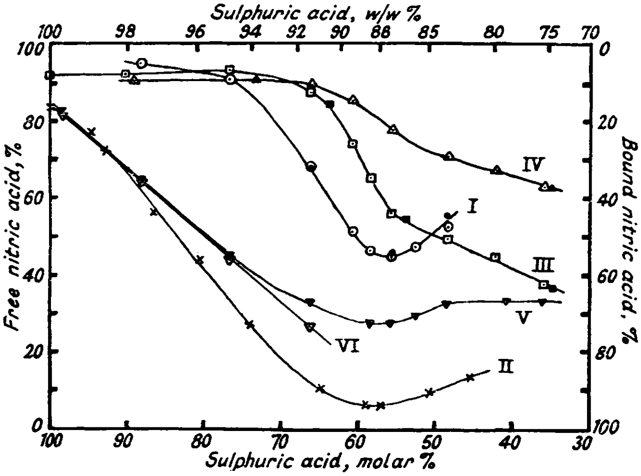
---

* Part IV, *J.*, 1953, 1998.

urea was far less favourable. The urethanes behaved differently. Here (curves III and IV), though the 88—85% w/w sulphuric acid region clearly marked a transition point in the curves, the proportion nitrated at equilibrium continued to increase in more dilute acid.

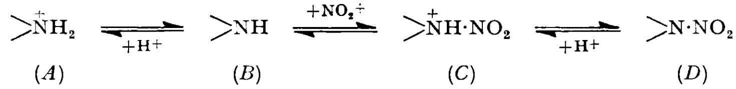
The qualitative difference between urea (or guanidine) and the urethanes may be due to differences in the nitration processes involved, or to differences in basic strength which might affect the nitration equilibrium. We do not favour the first of these hypotheses, though solely on the evidence (see Part VI) that in a less acidic solvent, *viz.*, acetic anhydride, urethane and urea are nitrated at similar speeds.

Equilibrium proportions of nitric acid at 25°.



I.	Nitrourea, 0·2M	⊙
	Urea nitrate, 0·2M	●
II.	Nitroguanidine, 0·2M	×
III.	Nitrourethane, 0·2M	⊡
	Urethane and nitric acid, each 0·2M	■
IV.	*N*-Methylnitrourethane, 0·2M	△
	N-Methylurethane and nitric acid, each 0·2M	▲
V.	Hexahydro-1 : 3-dinitro-1 : 3 : 5-triazine nitrate ("P.C.X."), 0·2/3M	▼
VI.	Cyclonite, 0·2/3M	▽

The second hypothesis can be discussed in terms of the following equilibria which may be involved:



$$\underset{(A)}{>\overset{+}{N}H_2} \underset{+H^+}{\rightleftharpoons} \underset{(B)}{>NH} \overset{+NO_2^+}{\rightleftharpoons} \underset{(C)}{>\overset{+}{N}H\cdot NO_2} \underset{+H^+}{\rightleftharpoons} \underset{(D)}{>N\cdot NO_2}$$

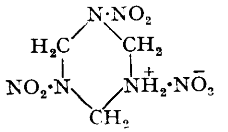
It has been shown by Wright (*Canad. J. Res.*, 1948, **26**, 104, 114) that *N*-nitration is dependent on the basic strength of amines, and it appears that the corresponding ammonium salts cannot, as such, be nitrated. It seems, however, that guanidine is nitrated as the guanidinium ion; the positive charge shared between three nitrogen atoms is presumably less discouraging to nitration than the localised charge in salts of simple amines. Charge distribution may also permit the direct nitration of salts of urea. But salts of urethane, like those of simple amines, might well be resistant to nitration; and it was thought that if allowance were made for the urethane removed from the nitration equilibrium by salt formation, then the resultant curve might resemble those obtained from guanidine and from urea.

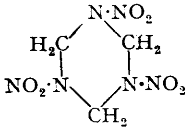
Cryoscopic measurements have therefore been made in sulphuric acid, and in sulphuric acid monohydrate. Urea and urethane gave identical depressions, within the limits of experimental error, in both solvents. In sulphuric acid (100% w/w) both were monoprotonated. In sulphuric acid monohydrate, a less suitable solvent, the indications were less precise; but the identity of their behaviour and the known basic strength of urea suggested that here, too, salt formation from urethane was essentially complete. Ultraviolet absorption spectra have also been examined but were not diagnostic; there was no significant absorption either in aqueous or in sulphuric acid solutions.

The evidence, therefore, does not support the second hypothesis. Unfortunately, the converse is not true: consideration of the equilibria involved shows that the cryoscopic measurements do not afford positive disproof. If suitable (and by no means improbable) values are postulated for the ratios B/A and $B/(C + D)$, then changes in the B/A ratio corresponding to small alterations in the percentage of ionisation of the base (as from, say, 99 to 98%) would greatly decrease the value of the ratio free nitric acid/bound nitric acid $[(A + B)/(C + D)]$. Such small alterations could not be detected cryoscopically.

We consider that further discussion is not yet warranted, particularly since (1) differences in the (unknown) basic strengths of nitrourethane and nitrourea (≡ differences in the ratio C/D) might be significant, and (2) we cannot exclude the possibility that a salt of urethane can be nitrated directly—*i.e.*, without passing through the base. Wright's work (*loc. cit.*) in acetic anhydride–acetic acid is rather far removed from the conditions we have employed; and it is to be noted that, even in 100% sulphuric acid, about 1/10th of the nitric acid potentially available from nitrourethane remains bound. We simply record, as evidence in favour of the second hypothesis (p. 3342), that urethane and *N*-methylurethane have been found, in water at least, to be much weaker bases than urea. This is at least consonant with our suggestion that, whilst urea is monoprotonated in 75—88% w/w sulphuric acid, the urethanes exist to a small, but varying, extent as free bases; and that the qualitative difference between curves I and II and curves III and IV is due to the less complete ionisation of the urethanes in more dilute (90 ⟶ 75% w/w) sulphuric acid.

(I)





(II)

When " P.C.X." (I) was dissolved in sulphuric acid of less than 80% w/w concentration, the nitric acid liberated corresponded simply to the nitrate content of the salt. In more concentrated (90—100%, w/w) sulphuric acid, nitric acid derived from the nitramino-groups was also liberated; if 3 molecular proportions of nitric acid are taken to be the potential (100%) yield, then as much as 82% of the total was liberated by 99·7% w/w sulphuric acid. Cyclonite (II) behaved similarly in concentrated (93—100% w/w) acid.

These results are presented graphically in the figure. The dip in the " P.C.X." curve around 88% w/w sulphuric acid is of particular interest. Here the free nitric acid found was less than that introduced, as nitrate, in the " P.C.X." It follows that in this region " P.C.X." must be partly converted into cyclonite: (I) and (II) are presumably in equilibrium. We have been able, using more concentrated solutions, to prepare cyclonite by the action of 88% w/w sulphuric acid upon " P.C.X."

Solutions of cyclonite, and of " P.C.X.," in sulphuric acid were not stable. Irreversible decomposition of the nitramino-groups occurs and, by equilibration, nitric acid is removed from the system. This explains why, apart from Part III of this series (*loc. cit.*), nitrous oxide, but not nitric acid, has been recognised as a product of the action of sulphuric acid upon cyclonite. Even in comparatively dilute (60% w/w) sulphuric acid, " P.C.X." was not indefinitely stable. After an induction period of *ca.* 10 hr. at 25°, a 0·067M-solution decomposed suddenly, and the nitric acid content fell, within an hour, from 0·065 to 0·005M. Irreversible decomposition is probably responsible also for the slight apparent difference between " P.C.X." and cyclonite in concentrated acid. Cyclonite, unlike " P.C.X.," dissolves slowly: the initial measurements could not be made so soon and the correction (see p. 3341) to zero time must be less reliable. In 91·5% w/w acid, 40 minutes elapsed before dissolution was complete and, though we report the value obtained, we regard it as only approximate.

EXPERIMENTAL

Materials.—The *N*-nitro-compounds were prepared by standard methods, or were given to us; for references and acknowledgments see Part III (*J.*, 1952, 1894).

*Preparation of Hexahydro-*1 : 3*-dinitro-*1 : 3 : 5*-triazine Nitrate* ("*P.C.X.*") (Hirst, Bevan, Carruthers, Dunning, Foss, Jones, and Sullivan, personal communication, 1943).—Freshly purified nitric acid (free from nitrous acid, 160 ml. of 98%) was placed in a 500-ml. bolt-head flask fitted with a mechanical stirrer, and cooled to −10° with acetone–carbon dioxide. Water (13·4 ml.) was added dropwise (temp. $<0°$), and the diluted (*ca.* 93%) acid then cooled to −40°. Hexamine dinitrate (20 g.) was added in 1 min. at −40°, and nitrolysis allowed to proceed for 10 min., in all, at −40°. Water (340 ml.) was then added streamwise in 7 min. with maintenance of the temperature at $<-10°$. The suspension in diluted acid was allowed to age, without cooling, for 5 min., and the prisms of *hexahydro-*1 : 3*-dinitro-*1 : 3 : 5*-triazine nitrate* (9 g.; m. p. 99°, decomp.) were collected on sintered glass, and washed with cold 50% nitric acid (twice), cold alcohol (twice), and ether (thrice) [Found (Hirst *et al.*): C, 15·1; H, 3·5; N, 34·6. $C_3H_7O_4N_5,HNO_3$ requires C, 15·0; H, 3·3; N, 35·0%]. Potentially available methylenedinitramine has been determined (*J.*, 1946, 1656), and the purity of the present sample was checked by the determination (with $FeSO_4$–HCl) of NO_3^- liberated in water or in aqueous sodium hydroxide (Found: NO_3^-, 25·6, 25·8. Calc.: NO_3^-, 25·8%).

Preparation of Solutions in Sulphuric Acid–Water Media, and Analysis.—The solutions were made and analysed by Simkins and Williams's method (*J.*, 1952, 3086). In this analysis nitrate is reduced to nitric oxide, in the absence of air, by boiling with an excess of standard ferrous sulphate in hydrochloric acid with ammonium molybdate as catalyst; the reaction is completed by expelling nitric oxide, and the residual ferrous salt titrated with potassium dichromate. When nitric acid and the amide (*e.g.*, urethane) were used as initial materials, the former was first added, as pure concentrated (70%) nitric acid, to sulphuric acid of known strength, and allowance was made for the water thus introduced. With the exception of cyclonite, all the compounds dissolved rapidly (<1 min.) in the solvents employed on being shaken by hand at room temperature; and the resultant solutions were brought to 25° within 5 min. of the start of the experiment.

Nitrourethane, *N*-methylnitrourethane, and nitrourea were destroyed (as was nitroguanidine in the paper cited) by boiling aqueous sodium hydroxide. If not so destroyed they affected the analysis, giving spurious indications of, respectively, 2, 17, and 2% of nitric acid. Cyclonite did not affect the analysis, but gave spurious indications of nitric acid after treatment with aqueous sodium hydroxide. "P.C.X." gave one molecular proportion of nitric acid with, or without, such treatment. Refluxing with aqueous sodium hydroxide was, therefore, not employed in the investigation of cyclonite or "P.C.X."

We employed the electrometric "dead stop" end-point in the titration of excess of ferrous sulphate with potassium dichromate, but have used Foulk and Bawden's simple circuit (*J. Amer. Chem. Soc.*, 1926, **48**, 2045), in conjunction with a Cambridge spot galvanometer (sensitivity 170 mm./μA): the end-point could be determined to $\pm 0·01$ ml. Our blank correction for the loss of ferrous ion was greater than that reported by Simkins and Williams, but was consistent at $0·0043 \pm 0·0002$M-nitrate.

Analytical Results.—In the Tables which follow our results are reported to 0·0001M-nitrate ($\equiv$0·01 ml. titration), but individual values are not printed for experiments in which the nitric acid content remained essentially constant ($\pm$0·001M) throughout: we consider the errors in analysis to be in most cases $<$0·0005M. Times (*t*, in min.) were measured from the initial mixing. The equilibrium values were obtained, as already described (p. 3341) by extrapolation to zero time. No allowance has been made for the water taken up, or set free, in the process of equilibration. For example, in Expt. 10 (half-denitration) the equilibrium solution presumably consisted of urethane, nitrourethane, and nitric acid dissolved in sulphuric acid of 83·73% w/w (initial value, as reported, 83·64% w/w).

Preparation of Cyclonite from "P.C.X." and Sulphuric Acid.—"P.C.X." (0·5 g.) was added, in 2 min. at 25°, to sulphuric acid (5 ml.; 88·5%, w/w). After 15 min. at 25°, the solution was poured on ice (25 g.), and the cyclonite (0·11 g.; m. p. 203°, decomp., undepressed by mixture with authentic material) collected.

Comparative Basic Strength of Urea and Urethanes in Dilute Hydrochloric Acid.—Solutions (0·290M in sucrose; 0·504, 0·495, and 0·491M in hydrochloric acid and in, respectively, urea, urethane, and *N*-methylurethane) were kept at 25°. The rate of inversion was determined by polarimetry, and compared with that given by hydrochloric acid alone. In detail we followed

TABLE 1. *Molarity of free* HNO_3 *obtained from nitrourethane* (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 1. H_2SO_4, 100·0% w/w. Equil. val.: [HNO_3] 0·183 (*t* 15 to 90).

Expts. 2, 3. H_2SO_4, 97·58% w/w. Equil. val.: [HNO_3] 0·185 (*t* 15 to 88).

Expt. 4. H_2SO_4, 94·70% w/w. Equil. val.: [HNO_3] 0·187 (*t* 15 to 88).

Expts. 5, 6.* H_2SO_4, 91·46% w/w. Equil. val.: [HNO_3] 0·175.

t	14 *	20	25 *	33 *	34	43	45 *
[HNO_3]	0·1740	0·1736	0·1735	0·1729	0·1734	0·1728	0·1717
t	55 *	57	63	64 *	75 *	80	94
[HNO_3]	0·1719	0·1725	0·1716	0·1708	0·1699	0·1712	0·1699

Expt. 7. H_2SO_4, 89·47% w/w. Equil. val.; [HNO_3] 0·148.

t	17	27	37	46	56	66
[HNO_3]	0·1460	0·1457	0·1449	0·1436	0·1438	0·1420

Expt. 8. H_2SO_4, 88·46% w/w. Equil. val.: [HNO_3] 0·130.

t	19	28	40	50	61	70
[HNO_3]	0·1288	0·1284	0·1265	0·1266	0·1259	0·1251

Expt. 9. H_2SO_4, 87·26% w/w. Equil. val.: [HNO_3] 0·112.

t	19	32	45	57	72	83	97
[HNO_3]	0·1116	0·1117	0·1117	0·1104	0·1101	0·1091	0·1074

Expt. 10. H_2SO_4, 83·64% w/w. Equil. val.: [HNO_3] 0·099 (*t* 17 to 71).

Expt. 11. H_2SO_4, 79·88% w/w. Equil. val.: [HNO_3] 0·089.

t	16	26	36	47	56	67	76	86
[HNO_3]	0·0784	0·0864	0·0884	0·0880	0·0876	0·0874	0·0872	0·0869

Expts. 12, 13.* H_2SO_4, 75·38% w/w. Equil. val.: [HNO_3] 0·075.

t	13	28	37	50	60	72	82	90
[HNO_3]	0·0096	0·0209	0·0281	0·0366	0·0423	0·0479	0·0522	0·0552
t	112 *	133 *	159 *	192 *	221 *	277 *	401 *	
[HNO_3]	0·0619	0·0661	0·0695	0·0724	0·0738	0·0747	0·0747	

* In this and similar Tables, asterisks relate values of *t* to experiment numbers similarly marked.

TABLE 2. *Molarity of free* HNO_3 *obtained from urethane* (0·2M) *and* HNO_3 (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 14. H_2SO_4, 90·55% w/w. Equil. val.: [HNO_3] 0·169.

t	14	24	34	46	59	74	88
[HNO_3]	0·1681	0·1680	0·1671	0·1667	0·1658	0·1644	0·1644

Expt. 15. H_2SO_4, 86·40% w/w. Equil. val.: [HNO_3] 0·109 (*t* 15 to 75).

Expt. 16. H_2SO_4, 74·57% w/w. Equil. val.: [HNO_3] 0·073.

t	35	73	100	134	165	203	279	330
[HNO_3]	0·1289	0·1015	0·0909	0·0833	0·0793	0·0766	0·0751	0·0737
t	378	443	494					
[HNO_3]	0·0736	0·0730	0·0730					

TABLE 3. *Molarity of free* HNO_3 *obtained from* N-*methylnitrourethane* (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 17. H_2SO_4, 97·58% w/w. Equil. val.: [HNO_3] 0·181 (*t* 13 to 83).

Expt. 18. H_2SO_4, 94·70% w/w. Equil. val.: [HNO_3] 0·181 (*t* 12 to 80).

Expt. 19. H_2SO_4, 91·46% w/w. Equil. val.: [HNO_3] 0·179.

....	14	25	38	51	66	85
[HNO_3]	0·1782	0·1768	0·1776	0·1769	0·1768	0·1758

Expt. 20. H_2SO_4, 89·47% w/w. Equil. val.: [HNO_3] 0·171.

t	13	24	36	49	62	80
[HNO_3]	0·1702	0·1692	0·1684	0·1675	0·1669	0·1656

Expt. 21. H_2SO_4, 87·26% w/w. Equil. val.: [HNO_3] 0·156.

t	13	25	36	48	60	75	90
[HNO_3]	0·1556	0·1547	0·1543	0·1547	0·1536	0·1530	0·1500

TABLE 3.—*Continued.*

Expt. 22. H_2SO_4, 83·64% w/w. Equil. val.: [HNO_3] 0·142 (*t* 12 to 80).

Expt. 23. H_2SO_4, 79·88% w/w. Equil. val.: [HNO_3] 0·135 (*t* 11 to 72).

Expt. 24. H_2SO_4, 75·38% w/w. Equil. val.: [HNO_3] 0·126.

t	13	26	46	66	97	126
[HNO_3]	0·1182	0·1255	0·1256	0·1254	0·1253	0·1252

TABLE 4. *Molarity of free* HNO_3 *obtained from* N-*methylurethane* (0·2M) *and* HNO_3 (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 25. H_2SO_4, 93·78% w/w. Equil. val.: [HNO_3] 0·181 (*t* 12 to 75).

Expt. 26. H_2SO_4, 74·59% w/w. Equil. val.: [HNO_3] 0·125.

t	11	23	35	51	65	85	116
[HNO_3]	0·1305	0·1251	0·1243	0·1237	0·1233	0·1223	0·1206

TABLE 5. *Molarity of free* HNO_3 *obtained from nitrourea* (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 27. H_2SO_4, 97·58% w/w. Equil. val.: [HNO_3] 0·190 (*t* 13 to 92).

Expt. 28. H_2SO_4, 94·70% w/w. Equil. val.: [HNO_3] 0·182.

t	12	24	33	44	56	69	89
[HNO_3]	0·1808	0·1795	0·1776	0·1765	0·1761	0·1742	0·1712

Expt. 29. H_2SO_4, 91·46% w/w. Equil. val.: [HNO_3] 0·136.

t	12	22	32	45	59	70
[HNO_3]	0·1334	0·1300	0·1269	0·1238	0·1206	0·1169

Expt. 30. H_2SO_4, 89·47% w/w. Equil. val.: [HNO_3] 0·103.

t	13	28	38	48	57	75
[HNO_3]	0·0996	0·0956	0·0935	0·0908	0·0880	0·0835

Expt. 31. H_2SO_4, 88·46% w/w. Equil. val.: [HNO_3] 0·093.

t	11	22	35	50	63	82
[HNO_3]	0·0905	0·0880	0·0858	0·0819	0·0796	0·0745

Expt. 32. H_2SO_4, 87·26% w/w. Equil. val.: [HNO_3] 0·089.

t	12	21	35	48	60	73	90
[HNO_3]	0·0857	0·0849	0·0822	0·0801	0·0775	0·0745	0·0722

Expt. 33. H_2SO_4, 85·78% w/w. Equil. val.: [HNO_3] 0·095.

t	11	22	34	45	57	75
[HNO_3]	0·0810	0·0905	0·0891	0·0869	0·0848	0·0811

Expt. 34. H_2SO_4, 83·64% w/w. Equil. val.: [HNO_3], 0·105.†

t	12	23	38	51	67	86	120
[HNO_3]	0·0565	0·0878	0·0987	0·0995	0·0978	0·0957	0·0905

† Probably slightly low owing to slow equilibration (compare Expt. 37).

TABLE 6. *Molarity of free* HNO_3 *obtained from urea nitrate* (0·2M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 35. H_2SO_4, 91·46% w/w. Equil. val.: [HNO_3] 0·135.

t	10	20	30	41	56	71
[HNO_3]	0·1325	0·1293	0·1262	0·1234	0·1190	0·1152

Expt. 36. H_2SO_4, 87·26% w/w. Equil. val.: [HNO_3] 0·091.

t	12	24	35	46	56	75
[HNO_3]	0·0888	0·0857	0·0836	0·0815	0·0791	0·0751

Expt. 37. H_2SO_4, 83·64% w/w. Equil. val.: [HNO_3], 0·111.†

t	12	23	36	51	65	77	90	120
HNO_3]	0·1370	0·1203	0·1115	0·1066	0·1041	0·1021	0·1008	0·0975

† Probably slightly high owing to slow equilibration (compare Expt. 34).

TABLE 7. *Molarity of free* HNO_3 *from " P.C.X."* (0·2/3M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 38. H_2SO_4, 99·68% w/w. Equil. val. : [HNO_3] 0·165.

t	18	33	49	62	90	105
[HNO_3]	0·1480	0·1622	0·1650	0·1652	0·1645	0·1654

Expts. 39, 40.* H_2SO_4, 97·58% w/w. Equil. val. : [HNO_3] 0·129.

t	16 *	24	33 *	49	49 *	64	76 *	83
[HNO_3]	0·1153	0·1220	0·1260	0·1287	0·1292	0·1292	0·1271	0·1287
t	94 *	107 *						
[HNO_3]	0·1295	0·1283						

Expt. 41. H_2SO_4, 94·70% w/w. Equil. val. : [HNO_3] 0·090.

t	15	26	37	52	74	107	191
[HNO_3]	0·0891	0·0882	0·0877	0·0872	0·0844	0·0812	0·0761

Extp. 42. H_2SO_4, 91·46% w/w. Equil. val. : [HNO_3] 0·065.

t	18	30	55	73	92	115
[HNO_3]	0·0642	0·0624	0·0620	0·0608	0·0590	0·0584

Expt. 43. H_2SO_4, 88·46% w/w. Equil. val. : [HNO_3] 0·055.

t	17	35	47	68	98	131
[HNO_3]	0·0541	0·0507	0·0493	0·0476	0·0433	0·0415

Expts. 44, 45.* H_2SO_4, 87·26% w/w. Equil. val. : [HNO_3] 0·055.

t	11 *	15	28	44	60	89	110 *	140 *
[HNO_3]	0·0566	0·0548	0·0518	0·0499	0·0479	0·0453	0·0431	0·0356

Expt. 46. H_2SO_4, 85·78% w/w. Equil. val. : [HNO_3] 0·059.

t	13	26	41	62	87	120
[HNO_3]	0·0600	0·0564	0·0537	0·0516	0·0494	0·0467

Expt. 47. H_2SO_4, 83·64% w/w. Equil. val. : [HNO_3] 0·065.

t	11	21	36	53	72	102	129
[HNO_3]	0·0645	0·0627	0·0613	0·0591	0·0576	0·0547	0·0517

Expt. 48. H_2SO_4, 79·88 w/w. Equil. val. : [HNO_3] 0·066.

t	13	25	39	52	67	97
[HNO_3]	0·0657	0·0652	0·0648	0·0648	0·0634	0·0622

Expt. 49. H_2SO_4, 75·38% w/w. Equil. val. : [HNO_3] 0·066 (*t* 14 to 64).

TABLE 8. *Molarity of free* HNO_3 *obtained from cyclonite* (0·2/3M) *in sulphuric acid–water mixtures at* 25° ± 0·2°.

Expt. 50. H_2SO_4, 99·68% w/w. Equil. val. : [HNO_3] 0·162.

t	20	30	42	53	65	154
[HNO_3]	0·1533	0·1590	0·1624	0·1617	0·1614	0·1615

Expts. 51, 52.* H_2SO_4, 97·58% w/w. Equil. val. : [HNO_3] 0·127.

t	18	26 *	28	37 *	38	49 *	49	62
[HNO_3]	0·1128	0·1178	0·1201	0·1239	0·1239	0·1254	0·1260	0·1273
t	81 *	90	92 *	122 *				
[HNO_3]	0·1274	0·1264	0·1264	0·1273				

Expt. 53. H_2SO_4, 94·70% w/w. Equil. val. : [HNO_3] 0·088.

t	41	64	94	125	153	188	261
[HNO_3]	0·0837	0·0812	0·0781	0·0751	0·0724	0·0720	0·0598

Expt. 54. H_2SO_4, 91·46% w/w. Equil. val. : [HNO_3] 0·053.†

t	43	57	66	110	159	197	223
[HNO_3]	0·0511	0·0499	0·0496	0·0450	0·0455	0·0428	0·0411

† Value doubtful, owing to slowness of dissolution.

the method of Walker and Aston (*J.*, 1895, **67**, 576), and found 77, 100, and 99 for the percentage of hydrolysis of, respectively, urea, urethane, and *N*-methylurethane hydrochlorides. When concentration differences are taken into account, our value for urea hydrochloride is close to that previously recorded; and it appears that, by this method, the urethanes are at least 40 times weaker bases than urea.

Ultra-violet Spectra.—Carefully purified urea, urethane, or *N*-methylurethane showed no significant absorption ($\varepsilon < 0·5$; *i.e.*, log ε is negative) when dissolved in water, 1·0M-sulphuric acid, or "AnalaR" concentrated (98%) sulphuric acid, and examined over the range 230—400 mμ. The extinction coefficient rose in the region 230—200 mμ, but no differentiation between solutions in water and acid was possible.

Cryoscopic Measurements (By C. Holstead *and* P. A. H. Wyatt).—In an attempt to detect differences in the degree of ionisation of urea and the urethanes in sulphuric acid solutions, cryoscopic measurements were carried out in both sulphuric acid and its monohydrate. The general method of Gillespie, Hughes, and Ingold (*J.*, 1950, 2473) was followed throughout, but with a form of cell similar to that of Newman, Ruivila, and Garrett (*J. Amer. Chem. Soc.*, 1945, **67**, 704), incorporating a Beckmann thermometer and a mechanical stirrer. It was possible to repeat measurements to within about 0·002° when the conditions of supercooling and bath temperature were rigidly adhered to, provided that a damp cloth was wrapped around the upper parts of the apparatus as a protection against changes of laboratory temperature which could otherwise produce large errors.

(a) *Sulphuric acid as solvent.*

Expt. (i). Urea as solute : molality of added water 0·060.

Molality of urea (m)	0·01933	0·03937	0·06003	0·08202	0·1068
Depression (θ)	0·227°	0·468°	0·719°	0·987°	1·296°
No. of ions (ν)	2·02	2·06	2·06	2·08	2·09
,, ,, (ν')	1·96	1·98	2·00	2·00	2·02

Expt. (ii). Urea as solute : molality of added water 0·062.

m	0·02271	0·04431	0·06874	0·09541	0·1214
θ	0·269	0·527	0·821	1·154	1·487
ν	2·04	2·04	2·05	2·08	2·11
ν'	1·98	1·98	1·99	2·02	2·04

Expt. (iii). Urethane as solute : molality of added water 0·064.

m	0·01067	0·03331	0·05722	0·08046	0·1078
θ	0·129	0·404	0·708	0·994	1·343
ν	2·07	2·08	2·11	2·11	2·14
ν'	2·02	2·02	2·06	2·06	2·08

Expt. (iv). Urethane as solute : molality of added water 0·055.

m	0·02545	0·05053	0·07513	0·09991	0·1253
θ	0·302	0·605	0·905	1·219	1·551
ν	2·04	2·04	2·06	2·08	2·12
ν'	1·98	2·00	2·01	2·03	2·06

Expt. (v). *N*-Methylurethane as solute : molality of added water 0·066.

m	0·009031	0·02748	0·04776	0·06829	0·09035
θ	0·109	0·336	0·589	0·847	1·140
ν	2·06	2·09	2·12	2·12	2·16
ν'	2·01	2·03	2·05	2·07	2·10

(b) *Sulphuric acid monohydrate as solvent.*

Expt. (vi). Urea as solute.

m	0·05495	0·1208	0·1857	0·2451	0·2898
θ	0·226	0·520	0·853	1·214	1·495

Expt. (vii). Urethane as solute.

m	0·06122	0·1132	0·1642	0·2165	0·2673
θ	0·247	0·497	0·747	1·055	1·399

Expt. (viii). Nitromethane as solute.

m	0·1108	0·1669	0·2494	0·3308
θ	0·435	0·625	0·942	1·270

Sulphuric acid monohydrate required two slight alterations in technique : the best degree of supercooling was found to be 1·8° (instead of 1·5°), and seeding was necessary as crystallisation could not be induced by solid carbon dioxide. The results are tabulated above. All depressions are corrected for supercooling by using the factors 0·012 (H_2SO_4) and 0·011 (H_2SO_4,H_2O). When additional water is present, θ refers to the depression of the f. p. below that of the treated solvent.

The ν values recorded in experiments (i)—(v) have been calculated in the same way as those of Gillespie, Hughes, and Ingold (*loc. cit.*), with the assumption that no solvation occurs. It would be possible to bring all the values much nearer 2·00 by introducing other solvation assumptions, but since the basis of these calculations is open to objections (Wyatt, *J.*, 1953, 1175), no further elaboration of this kind is presented here, especially as the immediate object was to detect differences in behaviour between urea and the urethanes. The values obtained from the empirical expression $\nu' = \theta/6{\cdot}0m$ (*loc. cit.*) are, however, included. The figures clearly show that there can be no significant difference in the degree of ionisation of urea, urethane, and *N*-methylurethane, all of which are probably completely monoprotonated in 100% sulphuric acid.

In sulphuric acid monohydrate also urea and urethane show identical behaviour up to 0·22M, as can easily be demonstrated by plotting the data of experiments (vi) and (vii) on the same graph. The sensitivity of this test is, however, somewhat less than for 100% sulphuric acid, since the depression for a bisulphate which gives two ions in this solvent is only about 33% greater than for a non-electrolyte at 0·25M, because of the large concentration of HSO_4^- ions in the solvent. Nevertheless, at concentrations (>0·22M) sufficient for a difference to appear between urea and urethane, it is such as to make urethane appear a stronger base than urea. Since urea is almost certainly monoprotonated at this concentration of sulphuric acid, it is concluded that urethane cannot be un-ionized to any extent detectable by this method.

Nitromethane has been found to be a very satisfactory non-electrolyte for comparison in this work. The data of Expt. (viii), when recalculated on a mol.-fraction basis (as is most convenient for the concentrated solutions involved) and plotted on a graph of θ against $-(1-0{\cdot}0013\ \theta)\log_{10}N_1$, yield a slope of 77·0, which is equivalent to a conventional cryoscopic constant of 3·88° g.-mol.$^{-1}$ kg. This is in satisfactory agreement with the value 3·95° calculated from Rubin's calorimetric data (Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, 1944, p. 337).

THE UNIVERSITY, SHEFFIELD, 10.

[*Received, April* 11*th*, 1953.]