797. *Comparative Reaction Rates in Solid and in Liquid Sulphuric Acid–Water Mixtures.*

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Rate constants of two different reactions have been measured in liquid and in solid sulphuric acid–water mixtures at 0°. The occurrence in both cases of a more rapid reaction in the solid medium is discussed.

During a study of rate measurements on the cyclodehydration of anils of acetylacetone to 2,4-dimethylquinolines[1] in sulphuric acid at temperatures below 10° it was found that where solidification of the medium inadvertently occurred the reaction still proceeded to completion. In consequence, a comparative study was made of the rates of this reaction in the solid and in corresponding supercooled liquid media at the same temperature, 0°, with two anils, 2-*p*-toluidinopent-2-en-4-one and 2-anilinopent-2-en-4-one and two different acid–water mixtures. In all cases, the cyclodehydration in the solid media was approximately twice as fast as in the liquid medium (Table 1*a*). Rates in solid and in liquid sulphuric acid media of the denitration of nitroguanidines to guanidine and nitric acid[2] were compared similarly; those in the solid media were about four times greater

Table 1. *Rate constants (min.$^{-1}$) at 0° in solid (k_S) and supercooled liquid (k_L) sulphuric acid–water mixtures.*

(*a*) Cyclodehydration of anils (0·025M)

Compound *	I	I	II	II
%H_2SO_4	85·5	84·0	85·5	84·0
10^4k_S	6·4, 6·2	3·4	0·93	0·72
10^4k_L	3·2, 3·0	1·7	0·47	0·31

(*b*) Denitration of nitroguanidines (0·0074M)

Compound *	III	III	III	IV
%H_2SO_4	86·4	85·7	84·5	84·5
10^3k_S	7·15	6·72	5·23	5·80
10^3k_L	1·78	1·60	1·27	2·12

* I, 2-*p*-Toluidinopent-2-en-4-one; II, 2-anilinopent-2-en-4-one; III, 2-nitrimino-1,3-diazacyclopentane; IV, 4-methyl-2-nitrimino-1,3-diazacyclopentane.

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[1] Bonner, Thorne, and Wilkins, *J.*, 1955, 2351.

[2] Bonner and Lockhart, *J.*, 1958, 3852.

than in the liquid for both 2-nitrimino-1,3-diazacyclopentane and 4-methyl-2-nitrimino-1,3-diazacyclopentane as shown in Table 1*b*. Variation of the initial concentration of 2-nitrimino-1,3-diazacyclopentane did not markedly change the ratio k_S/k_L of the rate constants for the solid and the liquid state (Table 2). As these initial studies were confined to measurements at 0° the sulphuric acid–water mixtures were restricted to the range 81—86% sulphuric acid over which the freezing points have values between 2 and 8°.[3] The only other range in which freezing points are above 0° is 98—100% sulphuric acid, but denitrations were too fast for measurement in these acids while the cyclodehydrations which proceeded at fast but measurable rates did not give satisfactory results, largely owing to the tendency of the solid samples to melt partially during reaction. Lower temperatures, *e.g.*, —10° to —20°, might avoid this difficulty, but will introduce the hazard of spontaneous solidification of the supercooled liquid.

TABLE 2. *Denitration of* 2-*nitrimino*-1,3-*diazacyclopentane at different initial concentrations in* 84·5% *sulphuric acid at* 0°.

10^2 × Initial concn. (M)	0·74	0·89	2·90
$10^3 k_S$ (min.$^{-1}$)	5·13, 5·34, 5·23, 5·32	5·07	5·12
$10^3 k_L$ (min.$^{-1}$)	1·27	1·18	1·54

A feature common to both the cyclodehydrations and denitrations is that they proceed through protonated forms of the substrate. In cyclodehydration this is a doubly charged species[4] which reacts by a rate-determining closure of the side chain to either *ortho*-position, followed by rapid loss of a proton. The medium is involved in maintaining the equilibrium concentration of the fractionally small amount of diprotonated anil and in the subsequent removal of the proton from the reaction intermediate, but both these proton transfers are presumably as fast in solid media as in the liquid and in any case are not rate-determining. The more rapid ring closure in a solid medium may then be due to entropy; the " caged " anil molecule has a very limited translatory motion but the greater flexibility of the side chain leads to a higher proportion of collisions with the *ortho*-positions at which the closure is affected. This effect would be similar to that discussed by Fairclough and Hinshelwood[5] for bimolecular reactions in solution where the solute molecule is larger than the solvent molecule and the solvent has a high density. Under these conditions the solvent can assume a close-packed structure from which the solute molecules tend to be squeezed out in groups with a consequent large increase in the number of repeated collisions between pairs of solute molecules at the expense of fresh encounters.

Although the denitration of nitroguanidines in sulphuric acid–water mixtures has a more complex mechanism than the cyclodehydration, it is basically similar in that the ionic form of the substrate requires assimilation of a second proton for reaction to occur. The transition state appears to require the presence of the solvent species,[2] H_3O^+ and HSO_4^-, which are involved only in proton transfer to, and proton withdrawal from, the bivalent nitroguanidinium ion during its conversion into the guanidinium and nitronium ion. A significant difference between the liquid and the solid environment could arise as a result of this participation of solvent acid and base species in the denitration. In the liquid the doubly positively charged nitroguanidinium ion will have a preponderantly negatively charged ionic atmosphere while, in the solid state, the solid phase in this range of media is the monohydrate[3] H_2O,H_2SO_4 (or H_3O^+,HSO_4^-) which provides the most favourable balance of the acid and base catalysts as the environment of the reacting ion.

Evidently the study of bimolecular reactions in solid sulphuric acid–water mixtures will provide results of even greater interest than the two reactions reported here. Some preliminary investigations on the nitration of guanidine using guanidine nitrate to provide

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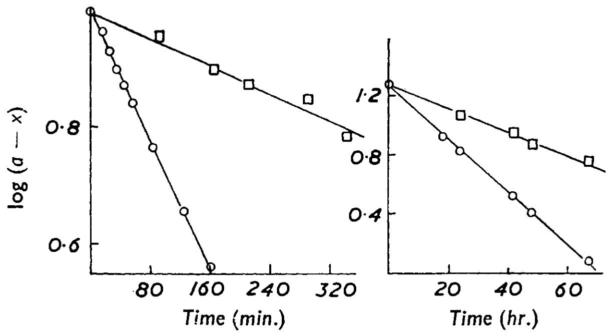
[3] Pickering, *J.*, 1890, 331.
[4] Bonner and Barnard, *J.*, 1958, 4176.
[5] Fairclough and Hinshelwood, *J.*, 1939, 593.

both reactants showed that the reaction was too fast for measurement even at 0° in the optimum range of sulphuric acid–water mixtures. The measurements did reveal, however, that the equilibrium was more rapidly attained in the solid than in the liquid medium.

EXPERIMENTAL

Materials and Media.—These were prepared as previously described.[1,2]

Kinetic Measurements.—For both cyclodehydration and denitration reactions, the reactant was weighed into a short tube made from a B24 cone. At zero time this tube was inserted into the neck of the flask containing the liquid sulphuric acid medium at 0° and shaken vigorously to dissolve the reactant as rapidly as possible. The flask was shaken in the bath at 0° for about 1 min. To ensure similarity of experimental conditions for both solid- and liquid-phase measurements, 2 ml. aliquot portions were successively removed without delay from the reaction solution and introduced into stoppered tubes, equal numbers of which were immersed in liquid air (to effect rapid solidification) and in a large vacuum flask containing ice and water. Each tube in the liquid-air bath was transferred to the ice-bath after complete solidification of the solution (which required about 1 min.) had occurred. In each experiment 5—8 samples each for the solid and liquid kinetic measurements were thus removed. At fixed time intervals, the stoppered tubes were taken from the ice-baths, and the contents diluted with water to stop further reaction and analysed in the usual way for the amount of unchanged reactant.[1,2] On rare occasions in the cyclodehydration, the supercooled sulphuric acid medium began to solidify during the initial mixing with the reactant. In such cases the experiment was repeated with the medium kept at about 5° before the addition of the reactant, and after complete dissolution of the latter the temperature of the solution was reduced rapidly to 0° by shaking for a few minutes in an ice-bath before removing the 2 ml. aliquot portions to the stoppered tubes. Since all reactions were extremely slow, this procedure did not introduce any detectable error.



A, Denitration of 2-*nitrimino*-1,3-*diazacyclopentane in* 85·7% *sulphuric acid; B, cyclodehydration of* 2-p-*toluidinopent*-2-*en*-4-*one in* 85·5% *sulphuric acid.*

☐ Liquid, ○ solid medium.

Simkins and Williams[6] have shown that the reversible denitrations in liquid sulphuric acid can be treated as a simple first-order change up to about 20% conversion of the nitroguanidine, and this procedure was followed here of plotting log $(a - x)$ against time; for liquid media good straight lines were obtained up to about 20% conversion, and for reactions in the solid media the straight line plot continued up to 50% conversion of the nitroguanidine. The cyclodehydration reaction was followed up to about 80% conversion. Typical results are shown in the Figure.

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[*Received, June* 19*th*, 1959.]

[6] Simkins and Williams, *J.*, 1952, 3086; 1953, 1386.