NOTES

Oxygen Tracer Experiments on the Reaction of NO_2 with Water

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In preparation for tracer work on the oxidation of nitrite ion in water, we have made oxygen tracer studies on the reaction of NO_2 with water, buffered or containing NaOH. The results of these experiments are shown in Table I. A considerable range of conditions was used in bringing the nitrogen dioxide in contact with the liquid phase. The experiments denoted as "high concn." were performed using NO_2 with only a small amount of carrier gas. In the series 1–7, bottled NO_2 was used and about 10% of N_2 by volume was present as carrier gas. In experiments 8–12, the NO_2 was generated by decomposing $Pb(NO_3)_2$, and thus it contains some oxygen, and considerably more carrier N_2 was used. In the experiments denoted as "low concn.," the NO_2 was cooled to Dry Ice temperature while N_2 was swept over it. The partial pressure of NO_2 is so low that a time of *ca.* 12 hours was required to build up the products to the level sought, about 0.01 *M*. In one experiment, the NO_2 was dissolved in CCl_4, and this solution was shaken with water. In the other experiments, the gas was introduced into the water through an 8 mm. tube, or by passing it through a sintered glass disk.

Table I

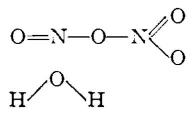
Oxygen Tracer Results on the Reaction of Nitrogen Dioxide with Water

(Room temperature, normal NO_2 added to water enriched in O^{18}; enriched NO_2^- present in experiments 7, 14 and 16, phosphate buffer for *p*H 7.)

Expt. no.	*p*H	Conditions	No. of O derived from NO_2[a] in NO_3^-	NO_2^-
1	14	High concn. in CCl_4	1.8	0.6
2	14	High concn., bubbled	2.0	0.8
3	14	High concn., bubbled	2.0	.9
4	14	High concn., bubbled	2.0	1.0
5	14	High concn., disk	1.0	0.3
6	7	High concn., disk	1.8	..
7	7	High concn., disk, 0.1 *M* NO_2^{*-}	1.0	..
8	14	High concn., bubbled	2.1	0.0
9	14	High concn., bubbled	2.0	0.0
10	14	High concn., bubbled	2.3	1.3
11	14	High concn., bubbled	2.4	1.2
12	14	High concn., bubbled	1.9	1.1
13	14	Low concn., disk	2.8	1.3
14	7	Low concn., disk, 0.1 *M* NO_2^{*-}	1.3	..
15	14	Low concn., bubbled	2.0	0.4
16	14	Low concn., bubbled, 0.5 *M* NO_2^{*-}	0.4	..

[a] For the method of isotopic analysis of NO_2^- and NO_3^-, see ref. 2.

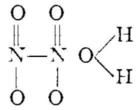
In experiment 13, the total NO_2^--oxygen found in the products equals within 3% of the maximum value of 4 derivable from N_2O_4. This means that the results for this experiment were not complicated by the exchange of reactants or products with the solvent, and the conclusion follows from the experiment that under the conditions which obtained for it, the activated complex has the unsymmetrical "nitrosyl nitrate" structure, with the base attacking the nitrosyl group



$$O{=}N{-}O{-}NO_2 \quad H_2O \qquad (1)$$

Experiments 10 and 11, in which the partial pressure of NO_2 was much higher than in 13, although not as high as in 2–9, provide some additional evidence for a nitrosyl nitrate activated complex.

A striking feature of the remaining data (excepting experiments 7, 14 and 16 in which labeled NO_2^- was added initially, and excepting experiment 5, which does deviate) is that the NO_2–oxygen content of the NO_3^- does not fall significantly below 2, although that for NO_2^- covers the range 1 + to 0. The reaction of NO_2 with water is known to be very rapid,[1] and the low values for the NO_2–oxygen content of NO_2^- can be attributed to the exchange of NO_2^- with water[2] in a region of local acidity comprised by the reaction zone. To explain the defect from three in the NO_2–oxygen content of the NO_3^- as being caused by exchange of NO_3^- in the reaction zone, would in view of the recurrence of *ca.* 2.0 NO_2–oxygens per nitrate over a considerable range of conditions require a remarkable series of coincidences. We feel rather that the results mean that there is a mechanism for placing one solvent oxygen in each nitrate formed, and that a strong exchange effect in the nitrate was operative only in experiment 5.[3] Attack by water in a configuration for $2NO_2$ corresponding to the symmetrical form of N_2O_4[4] would result in one solvent oxygen per nitrate



$$O_2N{-}NO_2 \quad H_2O \qquad (2)$$

Inherent in the experiments is the difficulty of controlling conditions at the scene of reaction. They do not make clear what factors favor an activated complex of the type of (2) over (1) but they do suggest that with water as reactant, (1) is operative only when the NO_2 is dilute. Reaction in the gas phase (water diffusing into NO_2 in gas) as compared to reaction in the liquid, may also favor one form over the other.

The reaction of NO_2 with ethyl alcohol is known[5] to yield mainly C_2H_5ONO and HNO_3, and thus it

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[1] P. G. Caudle and K. G. Denbigh, *Trans. Faraday Soc.*, **49**, 39 (1953).

[2] M. Anbar and H. Taube, This Journal, **76**, 6243 (1954).

[3] This exchange is known to be catalyzed by nitrous acid, C. A. Bunton, E. A. Halevi and D. R. Llewellyn, *J. Chem. Soc.*, 2653 (1953).

[4] The molecule in the solid has the symmetrical structure; J. S. Broadley and J. Monteath Robertson, *Nature*, **164**, 915 (1949).

[5] A. D. Yoffe and P. Gray, *J. Chem. Soc.*, 4112 (1951).

proceeds mainly by the unsymmetrical activated complex. Experiments we have done confirm this conclusion and extend it also to other alcohols. Two experiments were done for each alcohol, one without alcoholate ion, and one with alcoholate ion added. The reaction mixtures were made up to the same over-all composition by adding sodium alcoholate after reaction, also to the system which had none present during reaction. The NO_2 was introduced in CCl_4 solution, so that the reaction medium contained CCl_4 in volume equal to the alcohol. The average concentration of alcoholate ion was 0.6 *M*. The salt which separated after reaction was collected, washed, and the nitrite content determined.[6] The fraction (percentage) of the NO_2 converted to NO_2^- (corresponding to the alkyl nitrate as the co-product) for each alcohol, without and with Na alcoholate present was found as: EtOH, 0.025, 0.12; *n*-BuOH, 0.051, 0.095; *t*-BuOH, 0.051, 0.11. In each case the unsymmetrical cleavage is the predominant[1] process (to form RONO and $NaNO_3$), but in each case also, there is a distinct increase in the fraction forming the nitrate ester when the alcoholate ion is present. The difference between the mode of action of NO_2 with the alcohols, and that assumed for water under some conditions may be caused in part by the difference in rate of reaction. The rate difference was demonstrated by an experiment in which the oxide dissolved in CCl_4 was shaken with a solution containing 1 mole of water for every 100 of C_2H_5OH. After reaction, the solution was diluted with water and extracted with CCl_4. It was found that only $^1/_5$ of the NO_2 disappeared by the reaction which forms organic esters, so that the specific rate of reaction of the oxide with water exceeds that with alcohol by a factor of at least 400. In view of the rapid rate at which NO_2 reacts in the liquid, this ratio is probably much below the true value, because diffusion of water through the alcohol will have limited the extent of the reaction with water. The much lower rate of reaction of NO_2 with alcohol makes it seem possible that alcohol, but not water, allows time for rearrangement of N_2O_4 from a symmetrical (presumably the equilibrium structure) to an unsymmetrical structure. The increase in extent of the reaction to form NO_2^- and organic nitrate when alcoholate is present is consistent with this interpretation, because the ion may be expected to react more rapidly than the alcohol.

Experiments 7, 14 and 16 were performed to learn whether the exchange of NO_2^- with $NO_2(N_2O_4)$ is rapid enough to compete with the reaction of the oxide with water. All experiments agree in showing effects of the exchange of NO_2^- with NO_2, since the nitrate formed is found to be much closer to the isotopic composition of the NO_2^- (and of the solvent) than it is in experiments without added NO_2^{*-}. It is remarkable that the exchange of NO_2 with NO_2^- can compete in rate with the reaction of NO_2 with water, even though the NO_2^- is much less abundant than is water. The effects of this exchange appear to be little felt in the other experiments of Table I, although NO_2^- is delivered as product in isotopic composition approaching that of the solvent. No appreciable effect of the nitrite as a uniformly distributed product would be expected (the concentration of the nitrite product did not exceed 0.01 *M*) but there would seem to be the possibility of extensive exchange in a local reaction zone. However, the nitrite would be present as HNO_2 rather than NO_2^-, and this may account for the failure to observe any exchange effects caused by product nitrite.

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[6] H. A. Liebhafsky and E. H. Winslow, *Anal Chem.*, **11**, 189 (1939).

Further Studies of the Diffusion of Mixed Solutes with the Gouy Diffusiometer

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This note supplements previous diffusion data for dilute aqueous solutions of mixed solutes[1] by presenting experiments in which there was simultaneous diffusion of mixtures of (a) glycolamide and sucrose and (b) glycine and glycolamide. The latter experiment illustrates clearly that, when the ratio of the diffusion coefficients of the two simultaneously diffusing solutes is between 0.92 and 1.08, deviations of the Gouy fringes from their ideal positions are barely measurable. This problem of resolution is of major importance in interpreting diffusion experiments on proteins.

To aid in interpreting the second experiment, single-solute diffusion and refractive index data were obtained for the recrystallized sample of glycine; these data are also compared with previous measurements.[2,3] The notation of Akeley and Gosting[1] will be adopted and only the most important definitions repeated; hence constant reference should be made to this former work.

Materials, Solutions and Experimental Procedure

The same sucrose and glycolamide samples were used in these experiments as in work reported earlier.[1,4] A commercially available sample of C.P. glycine[5] was once recrystallized from conductance water, drained centrifugally and dried at 60° for 48 hours *in vacuo*. The procedure for making up solutions and calculating their molarities, *C*, has been described elsewhere.[1] In these calculations the following molecular weights were used: sucrose 342.296, glycine 75.068 and glycolamide 75.068. For the mixtures, solution densities, *d*, were measured in 30-ml. Pyrex pycnometers; also, using the apparent molal volumes, ϕ, in ml. per mole, given below[6,7] for aqueous solutions of single solutes, corresponding densities for these three component solutions were

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[1] D. F. Akeley and L. J. Gosting, THIS JOURNAL, **75**, 5685 (1953).

[2] M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

[3] L. G. Longsworth, *ibid.*, **75**, 5705 (1953).

[4] P. J. Dunlop and L. J. Gosting, *ibid.*, **75**, 5073 (1953).

[5] Obtained from Pfanstiehl Chemical Company, Waukegan, Illinois.

[6] F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

[7] G. Jones and S. K. Talley, THIS JOURNAL, **55**, 624 (1933).