[CONTRIBUTION FROM THE PENNSYLVANIA STATE COLLEGE]

Polarographic Behavior of Organic Compounds. V. Kinetics in a System Nitroester–Nitroölefin–Nitroalcohol

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The kinetics of the hydration of 2-nitro-1-butene have been measured and have been used in calculating the kinetics of the loss of the elements of acetic acid by 2-nitro-1-butyl acetate to form 2-nitro-1-butene which in turn reacts with water to form 2-nitro-1-butanol. The specific rate constants for these two reactions were evaluated at three temperatures for two *p*H values; the apparent activation energies at the two *p*H values were calculated. The use of polarographic technique permitted simultaneous measurement of the two equilibria.

During the investigation of the polarographic behavior of the ethers and esters of 2-nitro-1-butanol[1], the ease with which 2-nitro-1-butyl acetate loses the elements of acetic acid in weakly acidic and neutral solution manifested itself in the formation of a small wave which preceded the main reduction wave of the ester and which increased in magnitude with time. This small wave was identified as being due to 2-nitro-1-butene through the synthesis of this compound and the observation of its polarographic behavior. It was desirable to study the kinetics of this elimination reaction. The transformation of the acetate ester to the olefin in basic solution has been observed.[2] The elimination reaction is also shown by the formate.[1]

Direct study of the phenomenon was difficult because as the 2-nitro-1-butene was formed it hydrated to form 2-nitro-1-butanol which produces a polarographic wave whose half-wave potential is almost identical with that of the ester and hence is superimposed on the wave of the ester. Therefore, the kinetics of the hydration of 2-nitro-1-butene were studied first; this information was then used for the analysis of the kinetics of the more complicated case of the elimination reaction of the ester. There is a further complication, that in basic solution the 2-nitro-1-butanol as well as the ester form their respective aci ions which are not polarographically reducible in the potential range covered. Accordingly, the study of the kinetics of the reactions was limited to weakly acidic and neutral media.

Experimental

Materials.—The 2-nitro-1-butyl acetate was prepared by the standard method, using sulfuric acid as catalyst and benzene for the removal of water by azeotropic distillation; physical constants were: b.p. 102.5–103.5° (10 mm.), n^{20}D 1.4280 (lit. values, b.p. 103° (10 mm.), n^{20}D 1.4287[2]). The method of Blomquist and Shelley[3] was used to prepare 2-nitro-1-butene; b.p. 60° (50 mm.), n^{20}D 1.4360 (lit. values, b.p. 60.5° (50 mm.), n^{20}D 1.4356[3]).

Apparatus.—Potential-current curves were obtained using a Sargent Model XXI Polarograph in conjunction with a dropping-mercury electrode with a capillary constant of 1.60 mg.$^{2/3}$ sec.$^{-1/2}$ (open circuit) in 1 *M* potassium chloride at 25° (h = 73 cm.). Measurements were made in an H-type cell with saturated calomel electrode; the sample half-cell was water-jacketed and maintained at 25 ± 0.1° by means of an external water-bath equipped with a circulating pump. For measurements at 38 and 48° the whole H-type cell was enclosed in a glass envelope maintained within ±0.1° of the required temperature by an external water-bath and circulating pump.

Oxygen was removed from the cell medium before the electro-reducible material was added by bubbling with nitrogen which had previously been bubbled through sulfuric acid, alkaline pyrogallol, water and a sample of the cell solution. All cell solutions were stirred at a constant rate between polarograms which were taken at ten-minute intervals.

Buffer Solutions.—All components of the buffers were analytical grade chemicals tested for polarographically reducible impurities. The water used was distilled from permanganate in an all-glass apparatus and the 1,4-dioxane (Eastman Kodak Co.) was purified in the usual manner.[4] The buffer solutions were prepared as follows: 0.15 mole of disodium hydrogen phosphate and 0.5 mole of potassium chloride were dissolved in 95% water–5% dioxane solution and diluted to one liter. The calculated amount of solid citric acid was added to bring the *p*H to the desired value and the *p*H of the buffer was checked with a Beckman Model G *p*H Meter. The ionic strengths of the two buffer solutions were calculated to be 0.70.

Calibration curves (concentration in m*M* *vs.* diffusion current in μa.) were prepared for olefin, alcohol and ester at both *p*H values for 25° and 38° in the following manner: 50 ml. of the buffer solution in a 50-ml. volumetric flask was bubbled with nitrogen and equilibrated in temperature, a weighed quantity of the electroreducible material added, and the solution shaken and polarographed immediately. All calibration curves were straight lines at both temperatures and hence the calibration curves for 48° were assumed to be straight lines also. These curves were not used to calculate concentrations from diffusion currents since in the rate equation a ratio of two concentrations is used, units are eliminated and, hence, the diffusion current measured may be used directly as a measure of concentration.

Results and Discussion

The hydration of 2-nitro-1-butene to 2-nitro-1-butanol can be followed directly since both are polarographically reducible and hence their concentrations can be measured at various times; from these data specific rate constants can be calculated for the disappearance of the olefin and the appearance of the alcohol. The discrepancy between the amount of 2-nitro-1-butene reacted and the amount of 2-nitro-1-butanol formed is a measure of the 2-nitro-1-butene which is polymerized.[5] The polymer formed is probably a polynitro compound which, because of its high molecular weight and hence low diffusion coefficient, makes a negligible contribution to the diffusion currents measured. Plots of log $[a/(a - x)]$ *vs.* time from the usual first order rate equation gave straight lines for the reactions involving the disappearance of 2-nitro-1-butene, and the appearance of 2-nitro-1-butanol, indicating that both reactions are first order. The specific rate constants for these reactions, k_1 and k_2, respectively, are reported in Table I. With 2-nitro-1-butene at 25° it was not possible to measure the

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[1] W. J. Seagers and P. J. Elving, THIS JOURNAL, **72**, 5183 (1950).

[2] B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[3] A. T. Blomquist and T. H. Shelley, THIS JOURNAL, **70**, 147 (1948).

[4] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

[5] A. T. Blomquist, W. J. Tapp and J. R. Johnson, THIS JOURNAL, **67**, 1519 (1945).

TABLE I

SPECIFIC RATE CONSTANTS FOR THE HYDRATION REACTION OF 2-NITRO-1-BUTENE AND FOR THE ELIMINATION REACTION OF 2-NITRO-1-BUTYL ACETATE[a]

pH	T, °C.	k_1, min.$^{-1}$ × 10^2	k_2, min.$^{-1}$ × 10^2	k_3, min.$^{-1}$ × 10^3
5.0	25	1.24	..	0.52
	25	1.24	..	0.60
	38	1.78	1.71	3.03
	38	1.92	1.99	3.01
	48	3.22	2.26	4.62
	48	3.67	2.24	4.43
7.0	25	1.14	..	5.35
	25	1.03	..	5.20
	38	2.56	1.38	9.25
	38	2.24	1.44	10.4
	48	3.80	2.00	40.0
	48	4.25	1.51	32.1

[a] k_1 is the rate of disappearance of 2-nitro-1-butene; k_2 is the rate of appearance of 2-nitro-1-butanol; k_3 is the rate of disappearance of 2-nitro-1-butyl acetate.

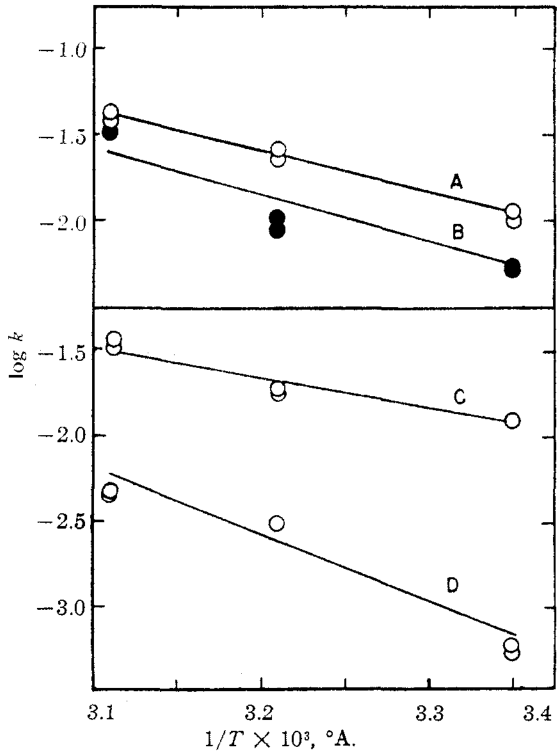

Fig. 1.—Plot of log k vs. 1/T: +2-nitro-1-butene at pH 5.0 (C), and at pH 7.0 (A); 2-nitro-1-butyl acetate at pH 5.0 (D) and at pH 7.0 (B).

rate of appearance of the 2-nitro-1-butanol since the wave is too small for accurate measurement even after 6 hours. At pH 5.0 the hydration reaction appears to overshadow the polymerization reaction since the rate of appearance of the alcohol almost equals the rate of disappearance of the olefin. At pH 7.0 the rate of appearance of the alcohol is only half that for the disappearance of the olefin. This would indicate that, since the polymerization reaction is known to be base catalyzed,[5] the hydration reaction must be acid catalyzed, as hydration reactions of olefins usually are. The disappearance of the olefin appears to be pseudo-unimolecular since one reactant, water, is present in large excess while the appearance of the alcohol is pseudo-unimolecular also since the hydration reaction is essentially irreversible.

In the elimination reaction of 2-nitro-1-butyl acetate the diffusion current of the combined wave of the ester and the alcohol can be corrected for the amount of alcohol produced by hydration of the olefin formed from the ester by using the value of k_2 for the appropriate condition.

In order to perform this operation a curve was plotted (current in μa., which represents the concentration of 2-nitro-1-butanol *vs.* time), using k_2 and the amount of olefin present at each particular time to calculate the abscissa. The area under this curve was calculated for each time interval, converted to the appropriate units and subtracted from the height, in μa., of the composite ester–alcohol wave. In this way a value for the concentration of 2-nitro-1-butyl acetate corrected for the amount of 2-nitro-1-butanol formed through hydration of the olefin was obtained for each time interval. From these data k_3, the rate of disappearance of the ester, was calculated (Table I). The elimination reaction appears to be pseudounimolecular. No previous mention of this reaction taking place in acid solution has been found in the literature.

The plot of log k *vs.* the reciprocal of the absolute temperature gave straight lines whose slope multiplied by 2.303R gives the apparent activation energy for the reaction involved; these results are plotted in Fig. 1 and summarized in Table II. The increase with increasing pH of the activation energy for the disappearance of the olefin and the decrease with increasing pH for the disappearance of the ester may be, in part, connected to the variation of the concentration of the bases present other than hydroxide ion, *i.e.*, citrate and phosphate species ions.

TABLE II

ACTIVATION ENERGIES FOR THE DISAPPEARANCES OF 2-NITRO-1-BUTENE AND 2-NITRO-1-BUTYL ACETATE

Compound	E, kcal. pH 5.0	E, kcal. pH 7.0
2-Nitro-1-butene	8	11
2-Nitro-butyl acetate	17	13

Acknowledgment.—This work was supported by a Frederick Gardner Cottrell Grant made by the Research Corporation to whom the authors wish to express their gratitude.

STATE COLLEGE, PENNA. RECEIVED AUGUST 7, 1950